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High Performing and Nitrogen-rich High Energy Density Materials

Dennis Fischer

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Erklärung

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Eidesstattliche Versicherung

Diese Dissertation wurde eigenständig und ohne unerlaubte Hilfe erarbeitet.

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(Dennis Fischer)

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Introduction

In the history of energetic materials till now there appears to be a trend proceeding from simple and readily available materials towards substances which need indeed five or more steps for their preparation. The early secondary explosives mainly consisted of mixtures of simple materials like nitrate esters, polynitrotoluenes and phenols, chlorates, nitrocellulose and ammonium nitrate. All those materials are formed in one or two steps from readily available and cheap materials.[1,2,3] After WW1 cyclohexamethylenetrinitramine (RDX) gained in importance since its detonation properties (D = 8750 m/s; $p_{C\text{-}J}$ 350 kbar)[4] are superior in comparison to the former used explosives. RDX is readily obtained via the nitration of hexamethylenetetramine.[5] Because of its simple preparation, chemical and mechanical stability and its good performance RDX is still the most frequently used military explosive to date. Efforts to replace RDX are ongoing today since the material is toxic to some extent and therefore a hazard to the environment.[9] In the course of research towards higher performing explosives other materials were discovered and developed. One of them is cyclooctamethylenetetranitramine (HMX) which is obtained under special nitrolysis conditions from hexamethylenetetramine.[6] HMX has a higher crystal density than RDX and therefore it performs slightly better.[4]

There are several strategies to increase the performance of an explosive material further since there are a series of parameters with a significant influence on the detonation properties. The detonation velocity (D) of the material is proportional to the loading density (ρ) and the detonation pressure ($p_{C\text{-}J}$) is dependent on the density of the material to the power of two. The equations for this were empirically determined by Kamlet and Jacobs with the constants K = 15.88, A = 1.01, B = 1.30.

$$p_{C\text{-}J}[\text{kbar}] = K\,\rho^2\Phi$$
$$D[\text{mm}\,\mu\text{s}^{-1}] = A\,\Phi^{0.5}(1+B\rho)$$

$$\Phi = N(M)^{0.5}(Q)^{0.5}$$

Φ is a parameter dependent on the number of moles of gas released (N) and the average molecular weight of the detonation products (M). Another important factor to $p_{C\text{-}J}$ and D is the heat of formation of the material since it contributes to the heat of explosion Q.[9]

One way of improving the performance of an energetic material is therefore to increase the density. Caged structures fulfill this requirement since they always crystallize in higher densities than their cyclic or linear analogs. The most prominent example among these structures certainly is hexanitrohexaazaisowurtzitane (CL-20) with a detonation velocity in the range of 9500 m/s and a detonation pressure in the range of 450 kbar.[4]

The hexaazaisowurtzitane cage can be accessed via the condensation of benzylamine and glyoxal in polar solvents. The major disadvantage of this reaction path is the substitution of the benzyl groups before nitrolysis which requires the use of a palladium catalyst in acetic anhydride. The aminal structure of the hexabenzylated cage is not stable in acidic media and fragments from it rapidly deactivate the catalyst which makes CL-20 a very expensive compound only used in special applications.[7] Other caged structures like octanitrocubane have been investigated but their synthesis is an expensive and laborious procedure and therefore they are only of academic interest.[8]

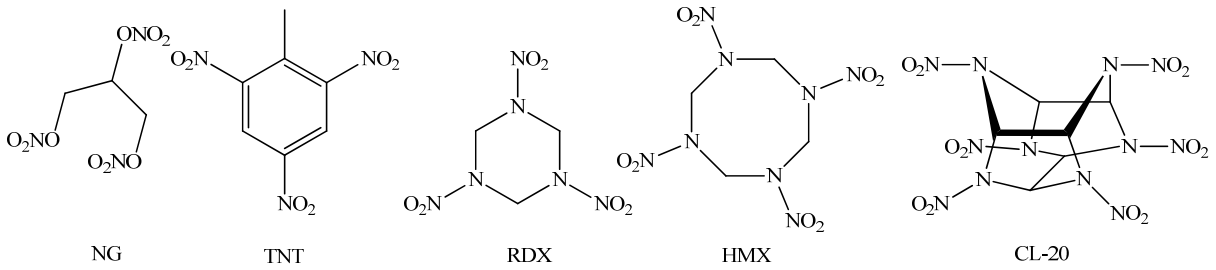

Figure 1: Prominent examples of secondary explosives: nitroglycerine (NG), 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), cyclotetramethylenetetranitramine (HMX), 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (CL-20).

Another strategy for the synthesis of high performing energetic materials is to maximize the heat of formation of the molecule. This can be done by using as much nitrogen in the molecule as possible connecting it with the highest number of N-N bonds possible. The gain in energy for every dinitrogen molecule released during combustion or detonation is very high since the difference in bond enthalpy between the N≡N triple bond and the N=N double bond is 527 kJ/mol and the difference between the N-N single bond and the N≡N triple bond is even 782 kJ/mol.[9] Compounds with a high heat of formation often have also one major drawback. The sensitivities of an energetic material are often correlated to its heat of formation and therefore the development of new high energy density materials (HEDMs) is often a tradeoff between the explosive power and the sensitivity towards friction and impact.[10]

Since these two requirements are therefore not likely to be fulfilled with one compound one goal in the research towards new HEDMs beneath the synthesis of non-toxic materials is to obtain materials with higher energy content but the same sensitivities like the previously used high performing HEDMs. Another research goal is the development of materials which are very insensitive towards impact and friction but still quite acceptable in their energetic properties for example 1,3,5-trinitro-2,4,6-triaminobenzene (TATB).[9] There are several chemical strategies for the reduction of the sensitivities of HEDMs including salt formation, push-pull systems and aromatic stabilization which play also an important role in the development of temperature stable explosives. Several insensitive and high temperature stable explosives are depicted in figure 2.

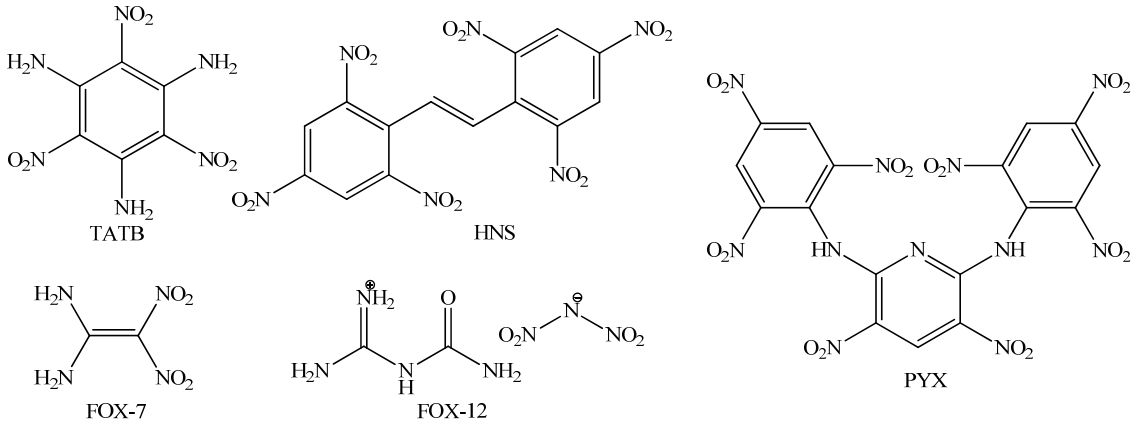

Figure 2: Prominent examples of less sensitive and/or high temperature stable secondary explosives: triaminotrinitrobenzene (TATB), hexanitrostilbene (HNS), diaminodinitroethylene (FOX-7), guanylureadinitramide (FOX-12) and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX).

Aromatic stabilization is an important tool in the development of high nitrogen containing HEDMs. Among the nitrogen-rich heterocycles with a high heat of formation useful in the synthesis of HEDMs the tetrazole ring is of special interest since tetrazoles combine good stability with simple methods of preparation. There are many tetrazoles with a nitrogen content higher than 80% and a considerable high thermal and mechanical stability. A few examples are depicted in figure 3.

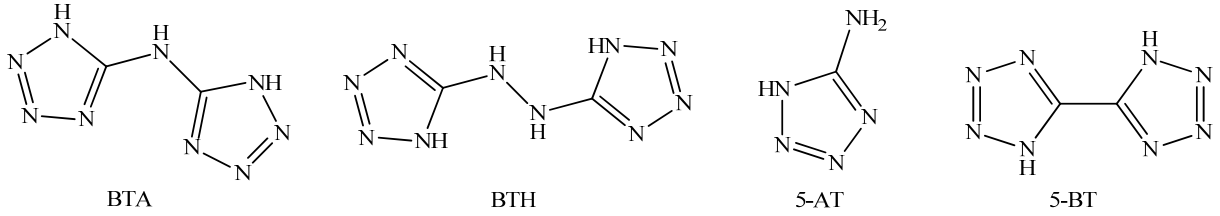

Figure 3: Examples for high nitrogen containing tetrazole derivatives: bistetrazolylamine (BTA)[11], 1,2-bistetrazolylhydrazine (BTH)[12], 5-aminotetrazole (5-AT)[13] and 5,5-bitetrazole (5-BT)[14].

The methods of preparation of tetrazoles involve simple methods like the 1,3-dipolar 2+3 cycloaddition of a nitrile with an azide or hydrazoic acid and the diazotization of an amidrazone or aminoguanidine derivative and subsequent ring closure (figure 4).[15]

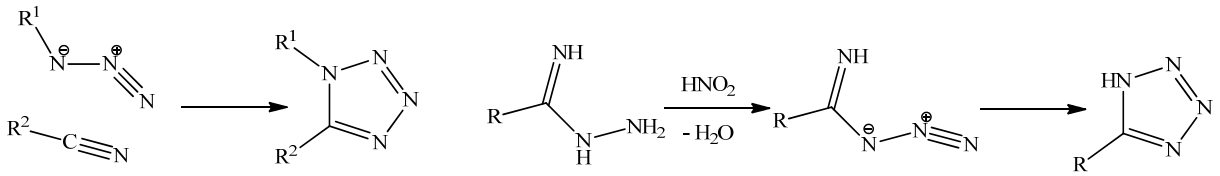

Figure 4: Two simple ways for the synthesis of tetrazole derivatives: 1,3-dipolar 2+3 cycloaddition and the diazotization of an amidrazone or aminoguanidine and subsequent cyclization.

Compounds with a high heat of formation only do not appear to be powerful explosives, since they are either poor performing and highly sensitive compounds or problems occur when these materials are tried to be initiated.[16] The solution to this problem is the synthesis of compounds with a suitable oxygen balance. This can be achieved by embedding oxidizing moieties like nitro and nitramino groups but also N-oxides.[17] Another method is to use heterocycles which are carrying their own "active" oxygen like furazanes (1,2,5-oxadiazoles) or furoxanes (1,2,5-oxadiazole-2-oxides). A few prominent examples of 1,2,5-oxadiazole(-2-oxide)s are depicted in figure 5.

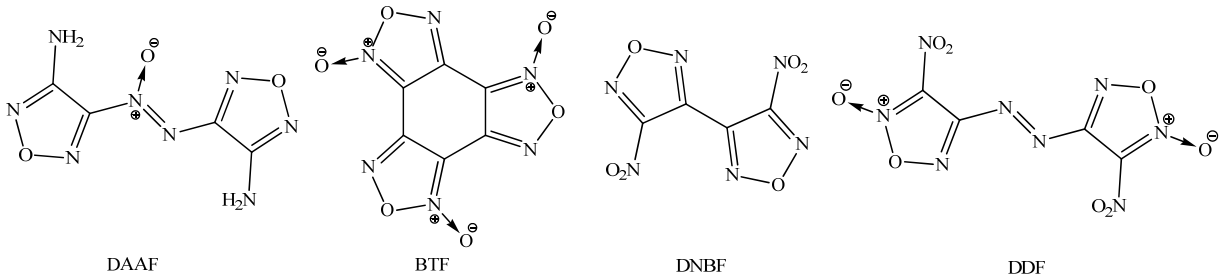

Figure 5: Examples for derivatives of 1,2,5-oxadiazole(-2-oxide)s: diaminoazoxyfurazane (DAAF)[18], benzotrifuroxane (BTF)[19], dinitrobifurazane (DNBF)[20] and dinitroazofuroxane (DDF)[21].

N-oxides can be introduced in tetrazole derivatives either by direct oxidation of the parent tetrazole with oxygen transfer reagents[22] or by cyclization of an azidoxime into a 1-hydroxy-tetrazole.[23] Nitramines are commonly introduced via the direct nitration of aminotetrazoles[24] and 5-nitrotetrazoles are often made via a *Sandmeyer*-type reaction from 5-diazotetrazoles with nitrite.[25]

Besides the tetrazoles there are other nitrogen containing heterocycles useful in the synthesis of energetic materials for example pyrroles[26], imidazoles[27], pyrazoles[28], (1,2,3- and 1,2,4-)triazoles[29], (mostly 1,3,5-)triazines[30], pyridazines[31], pyrimidines[32], pyrazines[33], and (1,2,4,5- and 1,2,3,4-)tetrazines[34] (figure 6).

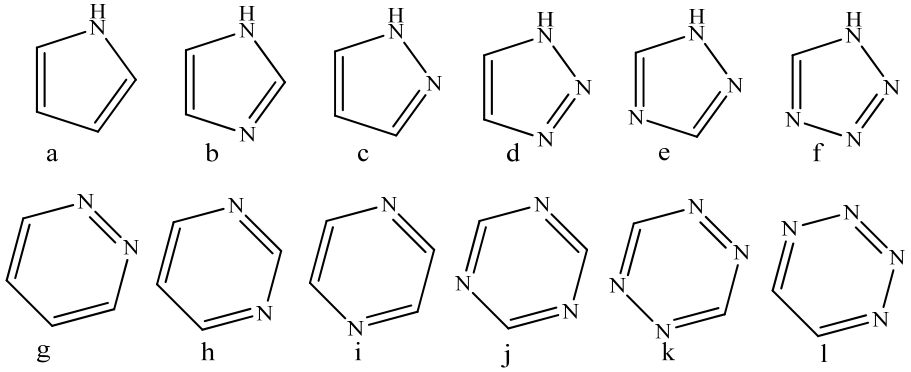

Figure 6: Nitrogen containing azoles and azines often used in the synthesis of energetic materials a) pyrrole, b) imidazole, c) pyrazole, d) 1,2,3-triazole, e) 1,2,4-triazole, f) tetrazole, g) pyridazine, h) pyrimidine, i) pyrazine, j) 1,3,5-triazine, k) 1,2,4,5-tetrazine, l) 1,2,3,4-tetrazine.

Among the not cyclic compounds containing a reasonable amount of nitrogen the guanidine structure plays an important role. Besides nitroguanidine which is an important ingredient in propellants there are several amino-/nitroguanidines important for the development of new HEDMs for example aminoguanidine[35], diaminoguanidine[36], triaminoguanidine[37], aminonitroguanidine[38] and dinitroguanidine[39].

The term HEDM does not only comprise secondary explosives but also primary explosives, propellants, and pyrotechnics. Regarding the primary explosives it has to be said that the main function of them is to quickly develop a detonation after being stimulated with any kind of activation energy. This property is often enabled or enhanced by the use of heavy metal salts. Sodium azide for example can be grinded in a mortar without any harm whereas lead azide would detonate violently. The same effect occurs with other anions like fulminate, acetylide and others. The heavy metal containing primaries and especially the widely used lead azide are currently tried to be replaced because of the toxic dusts which are formed during their detonation.[40] A way to replace the heavy metals is to use compounds with more N-N bonds which usually make the compounds more sensitive so that alkali salts are sufficient as cations. This concept yields highly endothermic and powerful but also sensitive compounds. The salt formation is still important since the desired thermal stability is achieved with deprotonation.

A special topic in the field of energetic materials research is the synthesis of agent defeat explosives. The idea is to generate an explosive which upon detonation releases a certain amount of disinfecting substances to destroy any agent which is part of a biological weapon in the first place.[9] These explosives typically contain NF_2[41] or SF_5[42] functional groups to release a certain amount of HF.

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Objectives

The objective of this thesis was to synthesize new high performing secondary but also heavy metal free primary explosives partially using the set of above mentioned building blocks and strategies with special attention on tetrazoleoxides, nitraminotetrazoles and 1,2,5-oxadiazole(oxides). The materials should be as simple and economic as possible in their preparation but also powerful energetics. The secondary explosives which are intended for the replacement of RDX ought to have an explosive power equal to or higher than RDX as well as sensitivities equal to or lower than RDX. The thermal stability of the new primaries and secondaries ought to be 200 °C or higher to enable a safe application and handling. Also the synthesis of other new exceptional HEDMs like oxidizers with a high oxygen content and compounds for agent defeat purposes is part of the research program towards modern HEDMs and was therefore treated in this thesis.

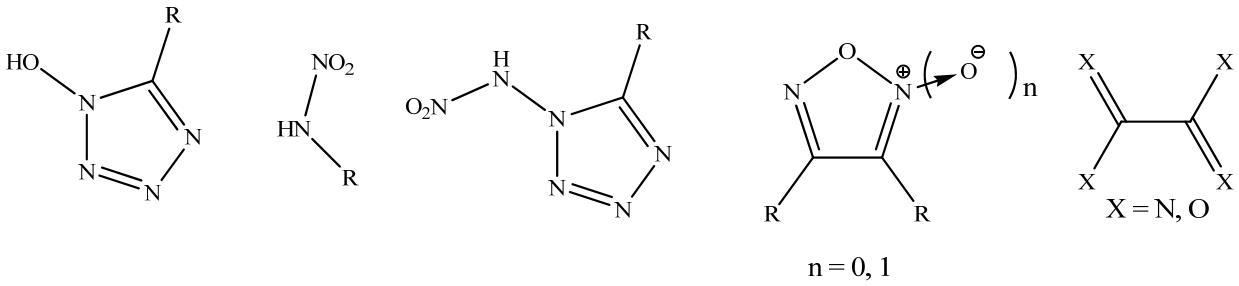


Figure 7: Important building blocks for this thesis.

Density enhancing synthetic building blocks (figure 7) are a substancial concept for this thesis. The carbazoyl moiety -C(O)NHNH- but also the nitramino functionality are important examples. Another concept is the C-C connection of sp2 carbon atoms especially to link two aromatic heterocycles together which is also improving the thermal stability of the molecules. Since N-oxide and especially tetrazoleoxide chemistry became an important topic to the group it was important to synthesize a series of unknown furoxanes and 1-hydroxytetrazoles. The improvement of the energetic power of tetrazoles can also be achieved introducing a nitramine attached at the ring nitrogen atoms and therefore the synthesis of a series of novel 1-nitraminotetrazoles is part of this thesis. The thermal stability of an acidic compound can be increased considerably through salt formation and therefore the purpose of this thesis was not the synthesis of novel covalent hydroxyl- and nitraminotetrazoles and other heterocycles alone but also the formation of energetic salts.

A major part in the development of new HEDMs is the investigation of their physicochemical properties. This comprises the measurement of temperature stabilities as well as sensitivity measurements towards impact, friction and electrostatic discharge. For the most promising compounds further tests have to be conducted. In the case of secondary explosives the “small scale shock reactivity test” has been established as an important tool for the proof of their explosive performance. In the case of primary explosives the most promising ones have to be tested for their initiation ability.

Summary

During the work for this thesis a synthesis towards a certain amount of new highly energetic tetrazole, furazane and furoxane derivatives but also other compounds was developed. The compounds were tested for their energetic properties and their suitability as primary or secondary explosives. Energetic derivatives belonging to the oxidizers and agent defeat explosives were also synthesized. A short summary about the synthesis is given below. The most important compounds of the thesis are displayed depicting their crystal structures.

1. Oxalylhydrazide nitrates

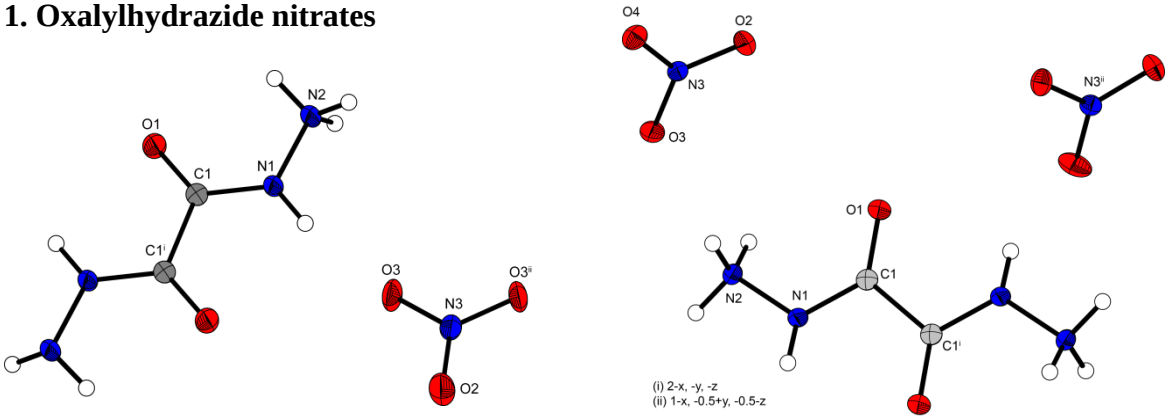


Figure 8: Crystal structures of oxalylhydrazinium nitrate and oxalylhydrazinium dinitrate.

In terms of simple preparation the nitrates of oxalylhydrazide (figure 9) are special since oxalylhydrazide can be readily precipitated quantitatively with hydrazine hydrate from a solution of diethyloxalate in alcohol. Protonation with dilute aqueous nitric acid yields the nitrates in good yield. The mononitrate combines a cheap and easy synthesis with an acceptable stability and performance. The N-N single bonds give a good heat of formation and the carbazoyl moiety leads to an acceptable density.

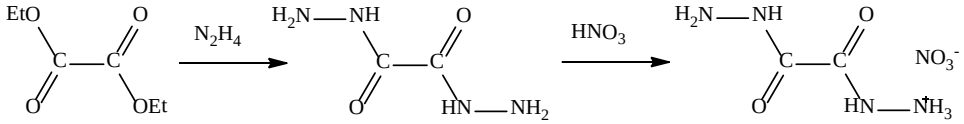


Figure 9: Synthesis of oxalylhydrazide nitrate.

Oxalylhydrazinium nitrate (OHN) and its dinitrate are probably two of the most easily and readily prepared secondary explosives out there. OHN combines an acceptable explosive performance (D = 8655 m s^{-1}, $p_{C\text{-}J}$ = 325 kbar) with moderate sensitivity (IS 11 J, FS > 360 N) and high thermal stability (T_{dec} = 273 °C).

2. Energetic salts of Tetrazolone

Combining the increase in density associated with the carbazoyl moiety with the heat of formation of tetrazoles leads to tetrazolone and its energetic salts (figure 10). Tetrazolone is readily available from 5-aminotetrazole.

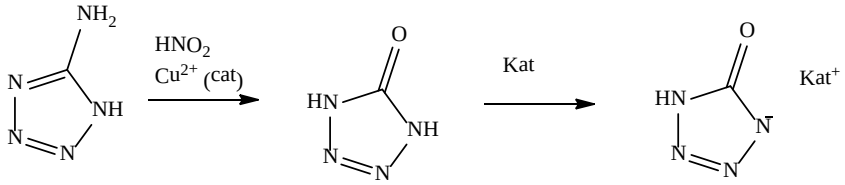


Figure 10: Synthesis of tetrazolone and energetic salts thereof.

3. Diaminonitroguanidine and 1-Amino-5-nitriminotetrazole

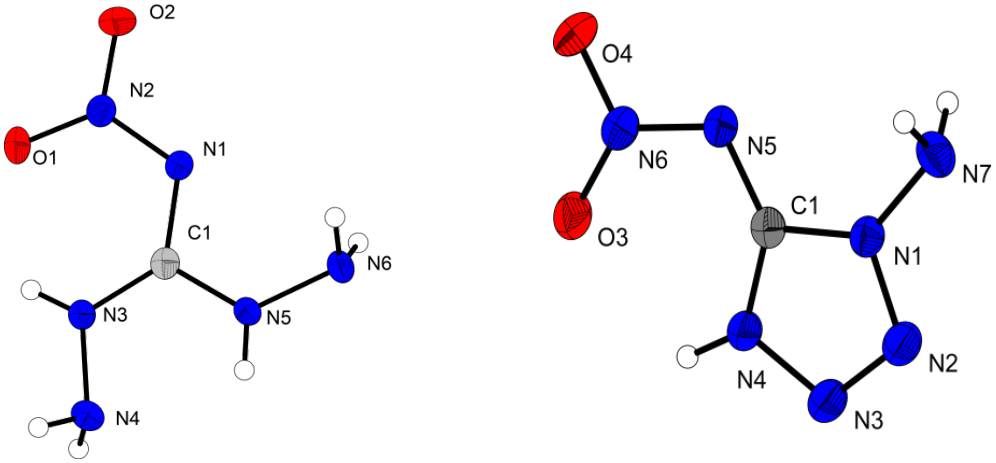


Figure 11: Crystal structures of diaminonitroguanidine and 1-amino-5-nitriminotetrazole.

Thinking about how to make tetrazoles more energetic N-amination certainly plays an important role in the synthetic strategy. The amination of 5-nitriminotetrazole was attempted several times but did not result in the desired molecule. Therefore another plan had to be taken in account. Starting with carbon disulfide it was possible to synthesize 1-amino-5-nitriminotetrazole via the literature known S,S'-dimethylnitrodithiocarbamate (figure 12). An important intermediate in this synthesis is the hitherto unknown diaminonitroguanidine. 1-amino-5-nitriminotetrazole is a highly energetic tetrazole derivative (D = 9340 m s^{-1}, $p_{C\text{-}J}$ = 419 kbar). Another unknown and highly energetic side product of the reaction of S,S'-dimethylnitrodithiothiocarbamate with hydrazine is dinitramino-1,2,4,5-tetrazine.

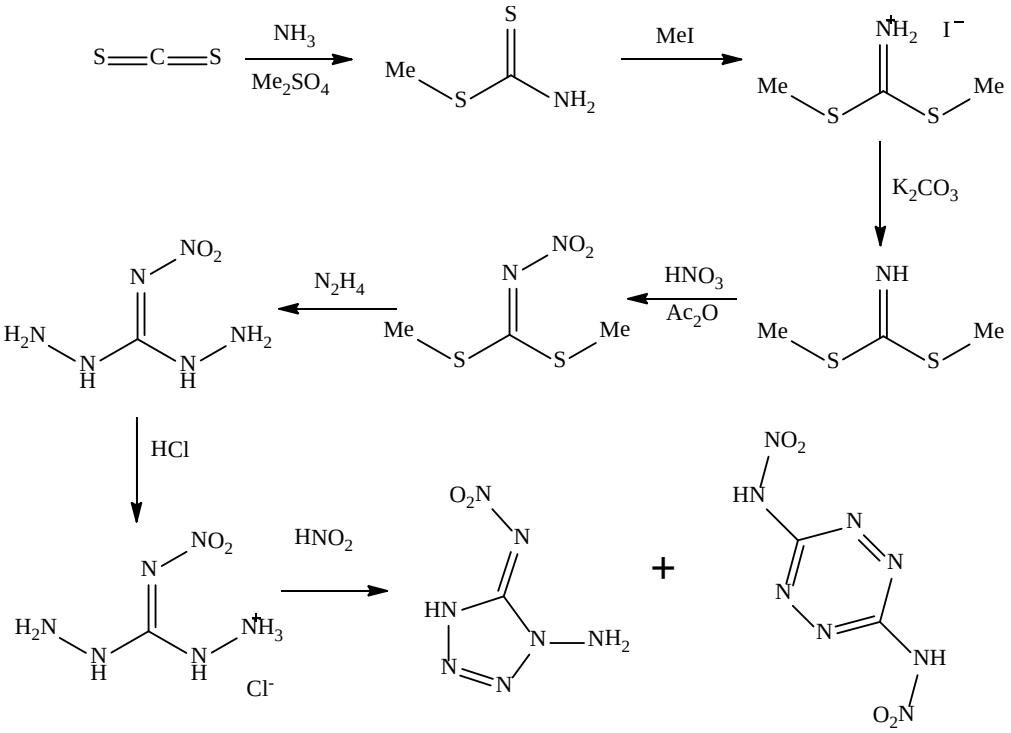


Figure 12: Synthesis of 1-amino-5-nitriminotetrazole and dinitramino-1,2,4,5-tetrazine.

4. Dihydroxylammonium 5,5'-bitetrazol-dioxide (TKX-50)

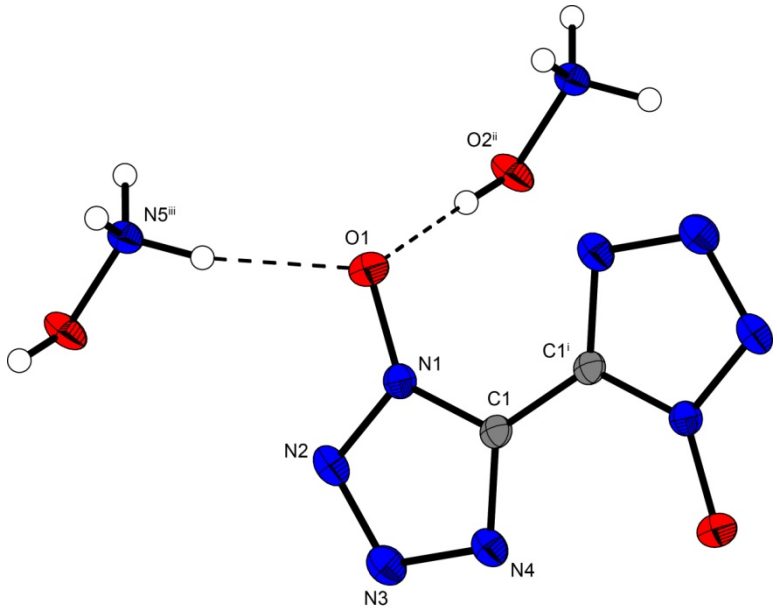


Figure 13: Crystal structure of dihydroxylammonium 5,5'-bitetrazol-dioxide **(**TKX-50).

The increase in density and oxygen balance of tetrazoleoxides compared to their parent tetrazoles was the reason to look into the salts of 1,1'dihydroxy-5,5'bitetrazole especially because C-C connected heterocycles have an increased density in comparison to their monocyclic analoga. This lead to the discovery of TKX-50, the high performing and relatively insensitive hydroxylammonium salt of 1,1'dihydroxy-5,5'bitetrazole. One major drawback is that the synthesis includes five steps and a very sensitive azidoxime intermediate (figure 14).

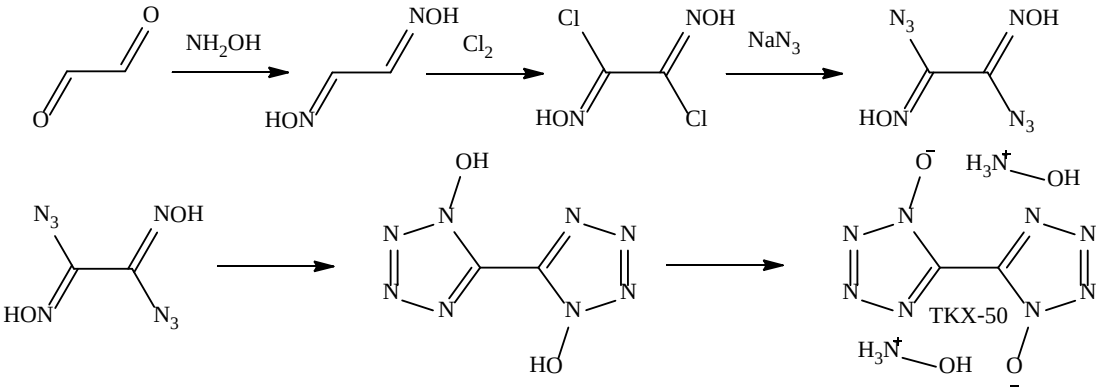


Figure 14: Synthesis of TKX-50.

TKX-50 is a good example of how salt formation can desensitize a high nitrogen containing molecule. The N-oxides provide an acceptable oxygen balance of −27% and cause a density of 1.877 g cm^{-3}. Sensitivity values of 20 J and 120 N as well as a calculated detonation velocity of over 9600 m s^{-1} and a detonation pressure of about 420 kbar are featuring the compound in a unique way.

5. 1-Hydroxy-5-aminotetrazole

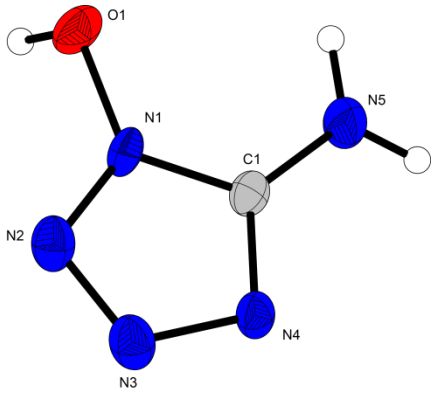


Figure 15: Crystal structure of 1-hydroxy-5-aminotetrazole.

One of the simplest and most fundamental energetic tetrazoles certainly is 5-aminotetrazole. Several attempts towards the synthesis of its N-oxide (oxidized either at N1 or N2) like direct oxidation or protection and subsequent oxidation did not lead to the desired results. The reaction between hydroxylamine and cyanogen azide finally lead to the hydroxylammonium salt of 1-hydroxy-5-aminotetrazole, a key intermediate in the synthesis of other energetic derivatives (figure 16). The synthesis of 1-hydroxy-5-aminotetrazole is very simple and not overly complicated in comparison with the synthesis of 5-aminotetrazole itself.

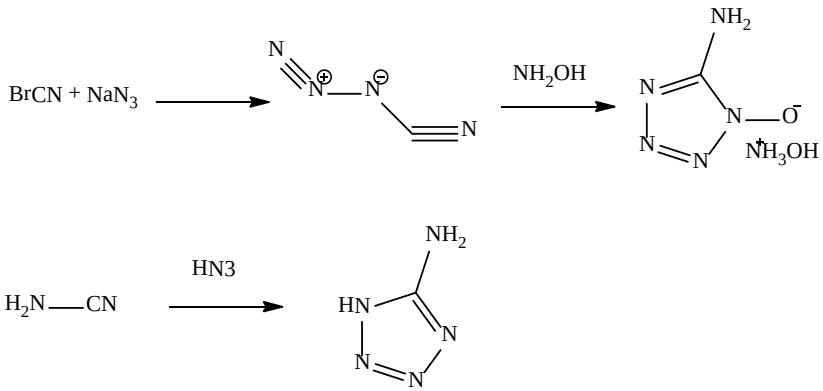


Figure 16: Synthesis of 1-hydroxy-5-aminotetrazole in comparison with 5-aminotetrazole.

The synthesis of 1-hydroxyaminotetrazole is a special achievement because ever since the research group was addressing tetrazole oxides the aminotetrazole oxides played a special role as starting materials for a variety of different possible target molecules.

6. 1,1'-Dihydroxy-5,5'-azobitetrazole

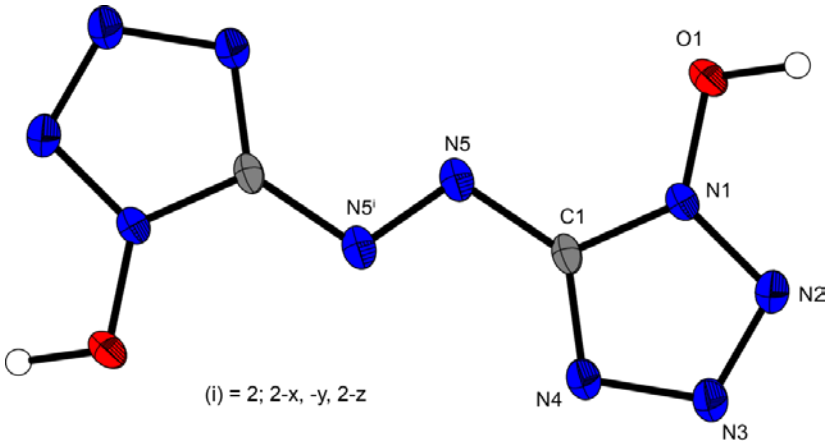


Figure 17: Crystal structure of 1,1'-dihydroxy-5,5'-azobitetrazole.

The salts of 1-hydroxy-5-aminotetrazole have an increased density and oxygen balance and are therefore more energetic than the salts of 5-aminotetrazole itself. The oxide decreases the thermal stability. More important than the energetic properties of 1-hydroxy-5-aminotetrazole is the fact that it is the starting material for another highly energetic tetrazole derivative. 5,5'-Azobitetrazole is playing an important role in the world of high nitrogen containing energetic compounds ever since it was discovered by Johannes Thiele in 1892. The molecule was synthesized for the first time from the reaction of 5-aminotetrazole with $KMnO_4$ in basic aqueous solution. The same reaction conditions lead to the salts of 5,5'-azobitetrazole (figure 18). The effect of the oxide is astonishing since the material is not only more energetic but also more thermally stable. N-oxidation of tetrazoles usually decreases the thermal stability of the material but the temperature stability of the 5,5'-azobitetrazole-1,1'-dioxide anion in non protic salts is higher than the one of the parent non oxidized azobitetrazolate. The 1,1'dihydroxy-5,5'azobitetrazole is even stable in its acidic form whereas the parent 5,5'-azobitetrazole is not. The reaction can be carried out with the crude hydroxylammonium 5-aminotetrazole-1-oxide since hydroxylamine is decomposing in hot alkaline solution anyway.

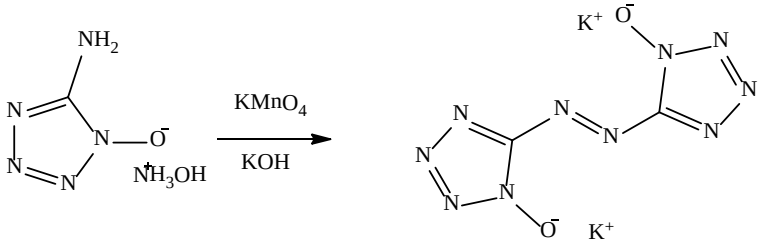


Figure 18: Synthesis of dipotassium 1,1'dihydroxy-5,5'azobitetrazolate.

7. 1-Hydroxy-5-nitriminotetrazole

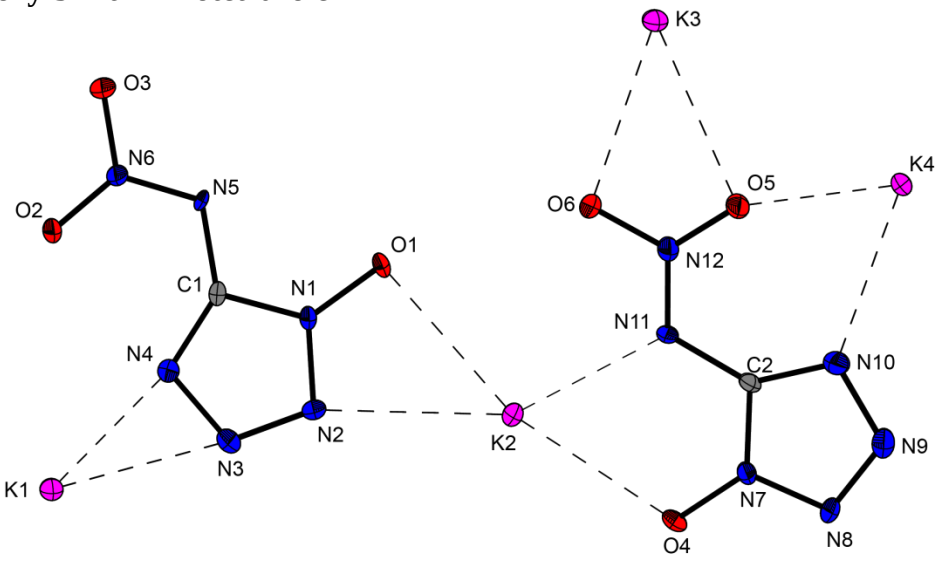


Figure 19: Crystal structure of dipotassium-5-nitriminotetrazole-1-oxide.

5-Nitriminotetrazole is an important energetic material derived from 5-aminotetrazole and can be accessed via direct nitration. One of the missing links in tetrazole-oxide chemistry was 1-hydroxy-5-nitriminotetrazole. Since direct nitration of 1-hydroxy-5-aminotetrazole did not result in the formation of 1-hydroxy-5-nitriminotetrazole the molecule had to be protected first. This was achieved with ethylchloroformate (figure 20). The salts of 1-hydroxy-5-nitriminotetrazole are certainly more energetic than the ones of the parent non-oxide but also less thermally stable. The dipotassium salt though possesses a remarkably high decomposition temperature of 320°C.

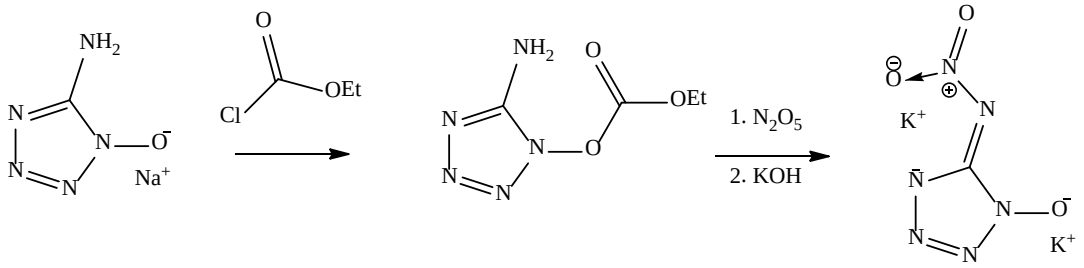


Figure 20: Synthesis of dipotassium 5-nitriminotetrazoleoxide.

8. Nitraminobifurazanes and Nitraminoazobifurazanes

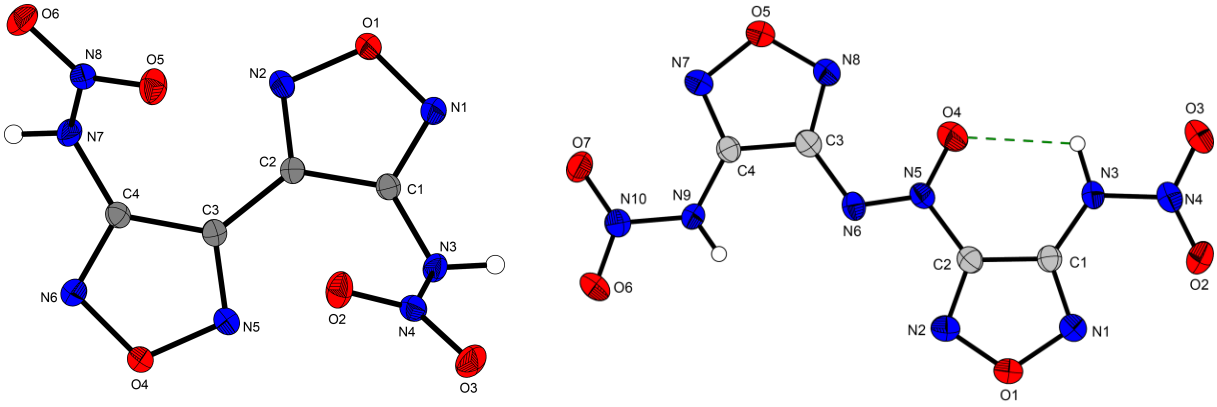


Figure 21: Crystal structures of dinitraminobifurazane and dinitraminoazoxybifurazane.

Diaminoazoxyfurazane is an important insensitive but energetic example of an explosive without any nitro moiety but still carrying its own active oxygen within the molecule. Nitration of this molecule and other bifurazanes increases the density, the oxygen balance and the number of N-N bonds (figure 22).

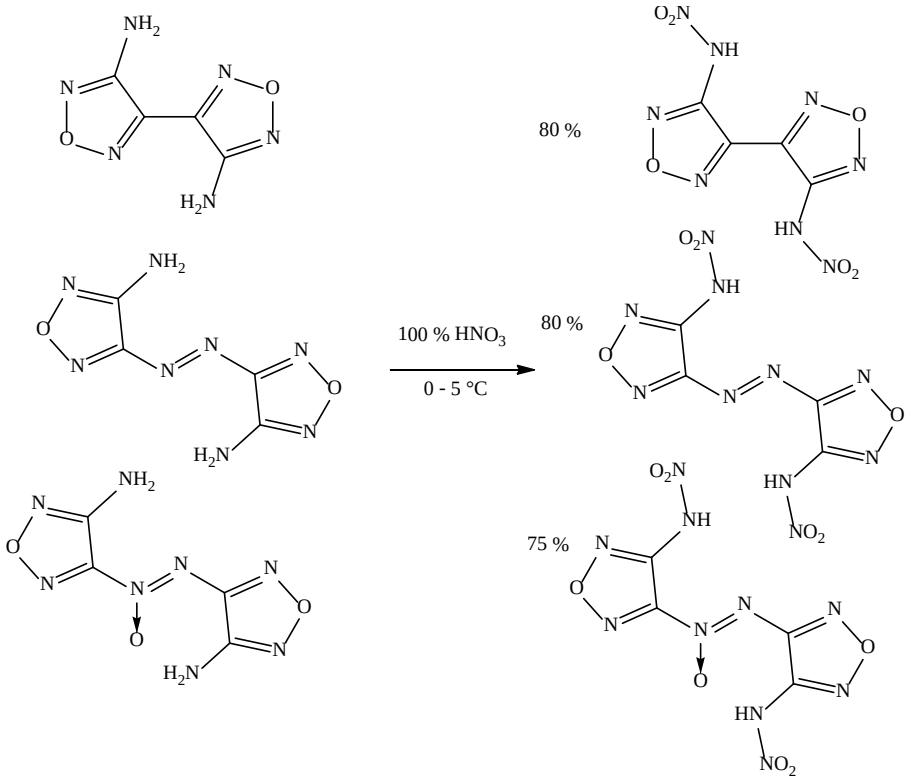


Figure 22: Synthesis of 3,3'-dinitramino-4,4'-bifurazane, 3,3'-dinitramino-4,4'-azofurazane, and 3,3'-dinitramino-4,4'-azoxyfurazane.

The dinitraminobifurazanes and dinitraminoazobifurazanes are highly energetic compounds with high densities and a good example of how the energy content and the density of a compound can be maximized with the introduction of nitro groups and N-oxides. The compounds are readily obtained from the parent amines after nitration in 100% nitric acid.

9. Bifuroxanes

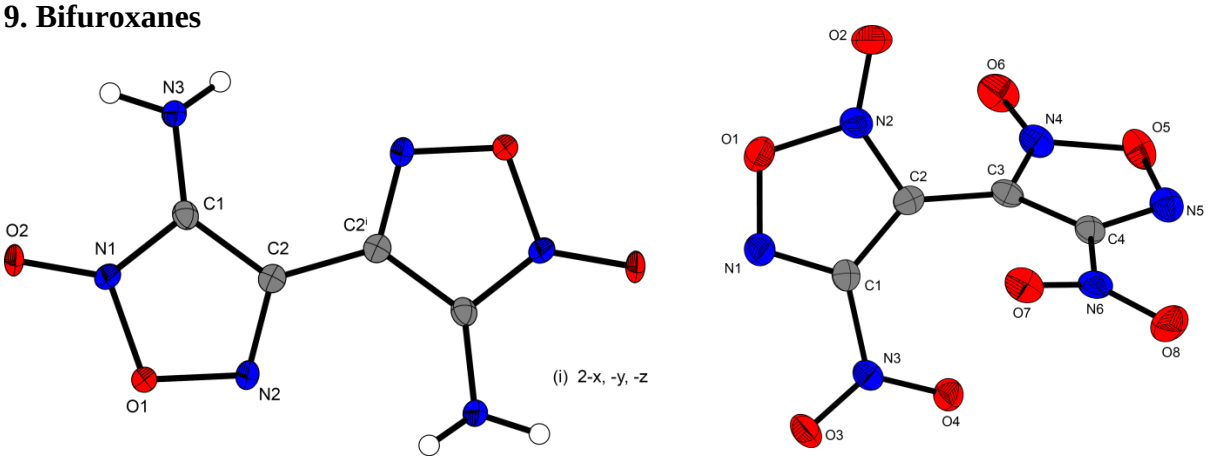


Figure 23: Crystal structures of 3,3'-diamino-4,4'-bifuroxane and 4,4'-dinitro-3,3'-bifuroxane.

Furoxanes are a very interesting class of energetic building blocks since they have a relatively high heat of formation but still carry their own “active oxygen”. Especially the chemistry of non annulated furoxanes is rich in unusual transformations. Therefore it is of special interest to synthesize the hitherto unknown 3,3’-diamino-4,4’-bifuroxane and its thermodynamic more stable isomer which is obtained after a rearrangement in refluxing dioxane (figure 24). With peroxysulfuric acid it was possible to obtain a small amount of 4,4’-dinitro-3,3’-bifuroxane which belongs to the class of the so called nitrocarbons. Because of its oxygen balance of 0 and its density of over 2 g/cm^3 the molecule represents a very high performing material.

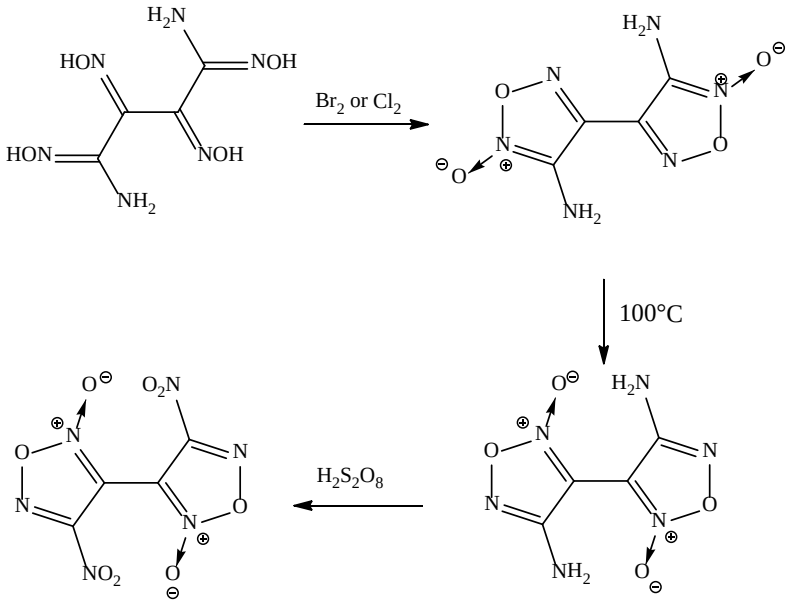


Figure 24: Synthesis of 3,3’-diamino-4,4’-bifuroxane, its isomer 4,4’-diamino-3,3’-bifuroxane and the very dense 4,4’-dinitro-3,3’-bifuroxane.

The diaminobifuroxanes represent a class of interesting energetic molecules which do not gain their “active oxygen” from nitro groups. The diamines are powerful explosives with a detonation velocity of over 8600 m s^{-1} and detonation pressures of over 340 kbar.

10. 3,4-Bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazole and 3,4-Bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazoleoxide

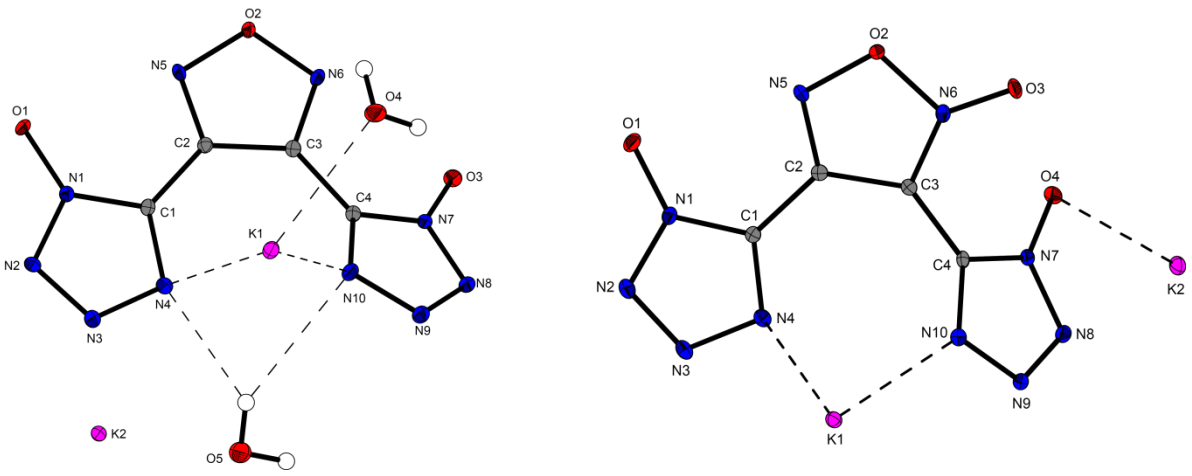


Figure 25: Crystal structures of dipotassium 3,4-bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazole dihydrate and dipotassium 3,4-bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazoleoxide.

The C-C connection of tetrazoleoxides and 1,2,5-oxadiazole(oxides) leads to compounds which combine the high heat of formation of tetrazoleoxides and the density enhancing properties of furazanes or furoxanes. Starting with the literature known dicyanofurazane and dicyanofuroxane it was possible to synthesize these molecules with amidoximes, chloroximes and azidoximes as intermediates (figure 26).

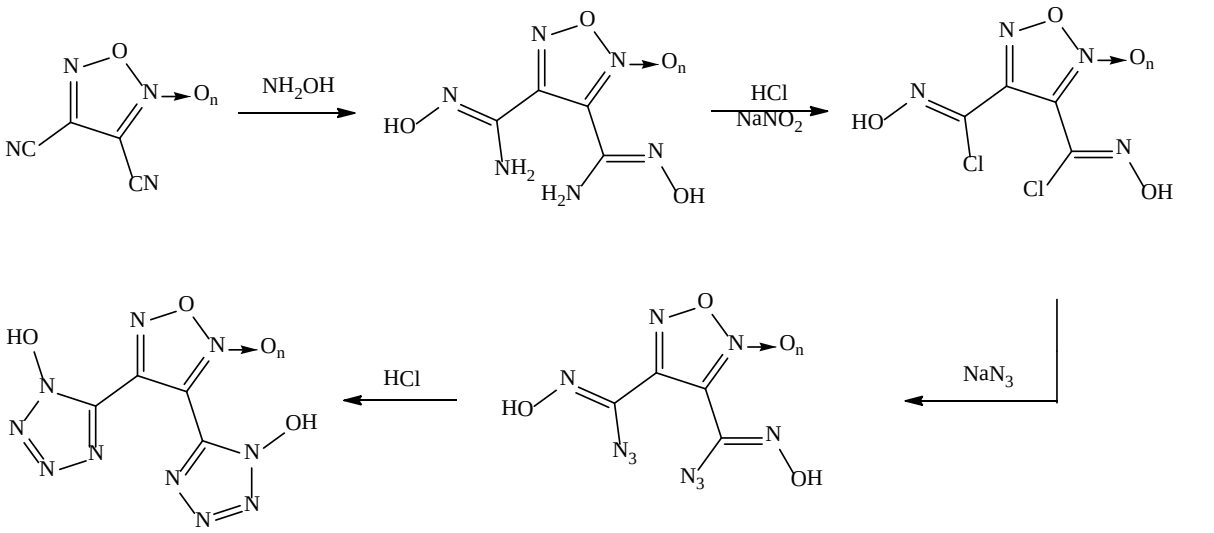


Figure 26: Synthesis of 3,4-bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazole (n = 0) and 3,4-bis(1-hydroxytetrazol-5-yl)-1,2,5-oxadiazoleoxide (n = 1).

11. Methylene bridged Nitropyrazoles

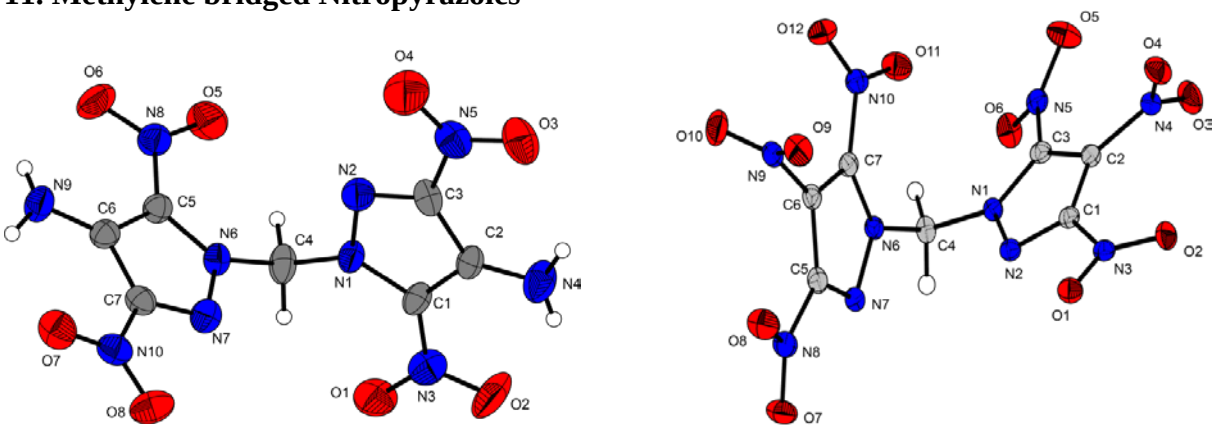


Figure 27: Crystal structures of bis(3,5-dinitro-4-aminopyrazolyl)methane (BDNAPM) and bis(3,4,5-trinitropyrazolyl)methane (BTNPM).

Not related to tetrazoles but also high performing explosives are the 3,4,5-trinitropyrazole derivatives. The connection of two heterocycles usually gives compounds with a higher density than the parent heterocycle alone. This concept was transferred to the nitropyrazoles, which were connected with a methylene bridge resulting in bis(3,5-dinitro-4-aminopyrazolyl)methane (BDNAPM). BDNAPM is a is a potential ingredient for high temperature stable insensitive munition because it decomposes at 310 °C. The oxidation of BDNAPM to the trinitropyrazole derivative using peroxysulfuric acid (figure 28) resulted in bis(3,4,5-trinitropyrazolyl)methane (BTNPM) which is an oxygen-rich explosive for potential use in aluminized mixtures comparable to HMX in its explosive power.

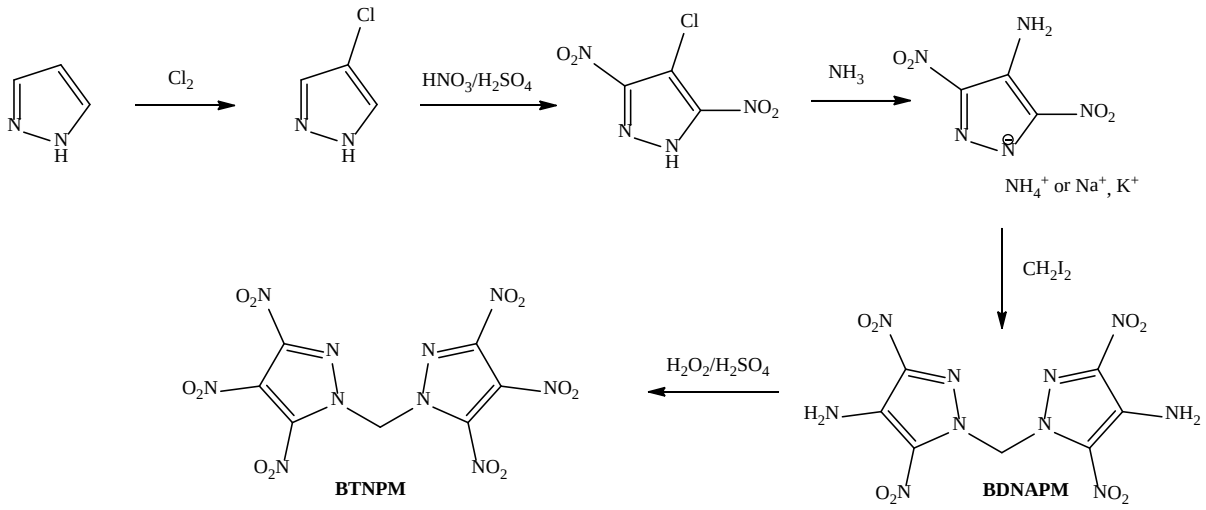


Figure 28: Synthesis of BDNAPM and BTNPM.

12. 1,5-Dinitraminotetrazole

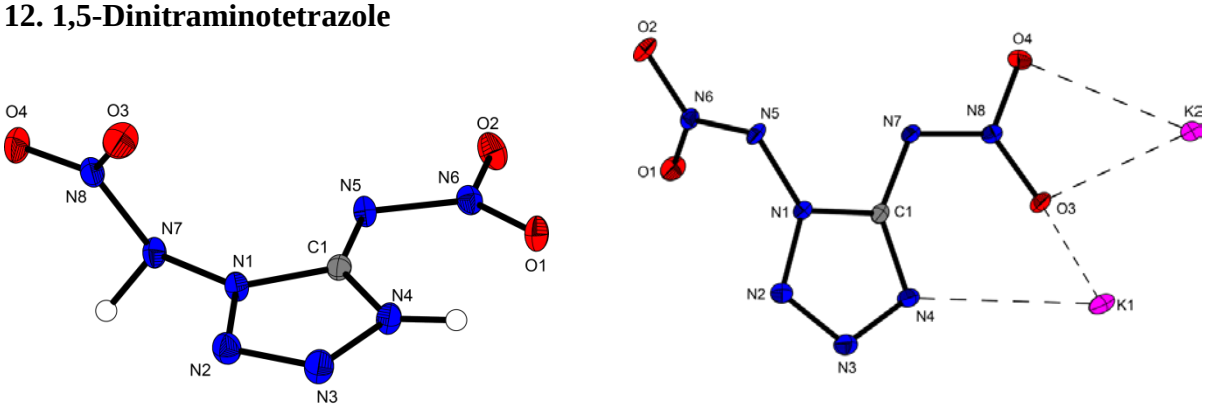


Figure 29: Crystal structures of 1,5-dinitraminotetrazole and dipotassium 1,5-dinitraminotetrazolate.

1-Amino-5-nitriminotetrazole and its salts are rather primary explosives and will probably find no application because of the complicated synthesis in this way. Thinking about how to make this molecule even more energetic leads to another important class of compounds, the 1-nitraminotetrazoles. The direct nitration of 1,5-diaminotetrazole to 1,5-dinitraminotetrazole was often tried but never successful. Another reaction path resulted in the desired molecule. The reaction of methylcarbazate with cyanogen azide resulted in a methoxycarbonyl protected 1,5-diaminotetrazole which can be nitrated easily with N_2O_5. Subsequent deprotection gives the dipotassium salt of the desired molecule (figure 30). The material and its salts are very sensitive towards friction and impact. Because of the high number of N-N bonds dipotassium 1,5-dinitraminotetrazolate is a powerful and heavy metal free primary explosive and it is stable up to 240°C.

1,5-Dinitraminotetrazole is a molecule which was believed to be a milestone in the chemistry of tetrazole derivatives. The synthesis was finally successful during the work for this thesis yielding indeed one of the most powerful CHNO explosives. The dipotassium salt of it is a good candidate as ingredient in heavy metal free priming mixtures.

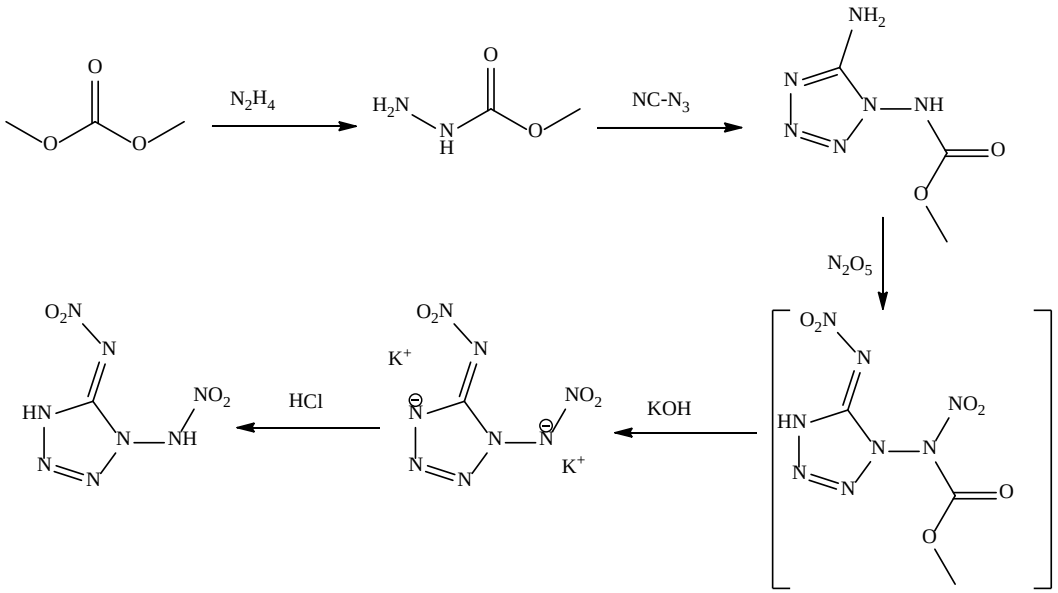


Figure 30: Synthesis of 1,5-dinitraminotetrazole.

13. 1,1’-Dinitramino-5,5’-bitetrazole

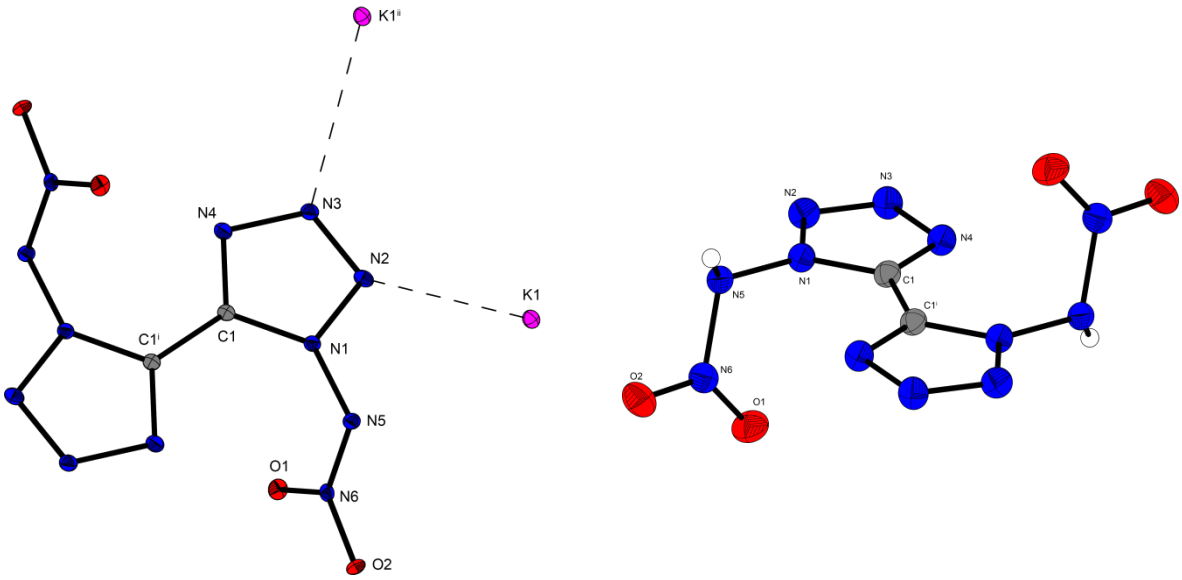


Figure 31: Crystal structures of dipotassium 1,1’-dinitramino-5,5’-bitetrazolate and 1,1’-dinitramino-5,5’-bitetrazole.

Another important representative of the 1-nitraminotetrazole series is 1,1’-dinitramino-5,5’-bitetrazole. Since 1-hydroxytetrazoles and 1-nitraminotetrazoles are similar in their chemical behavior the concept for the synthesis is similar to the synthesis of 1,1’-dihydroxy-5,5’-bitetrazole. Starting with glyoxal the synthesis had to proceed via a chlorohydrazide which is a stable precursor for the protected dinitrilimine. The chloride-azide exchange and subsequent cyclisation was done analog to the 1,1’-dihydroxy-5,5’-bitetrazole molecule (figure 32). The dipotassium salt of 1,1’-dinitramino-5,5’-bitetrazole is stable up to 200°C. Whereas dipotassium 5,5’-bitetrazole-1,1’-dioxide is a not very sensitive solid the dipotassium salt of the corresponding N-nitraminotetrazole is a very sensitive compound and certainly one of the most powerful and potent heavy metal free primary explosives to date.

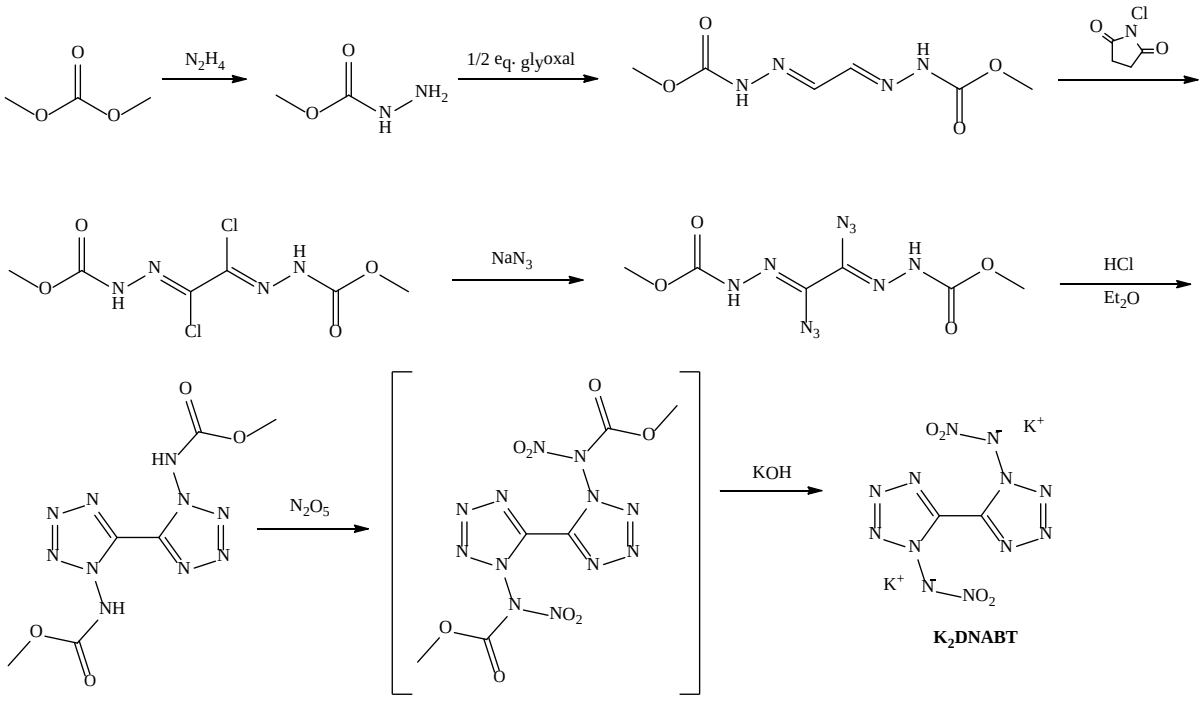


Figure 32: Synthesis of dipotassium 1,1'-dinitramino-5,5'-bitetrazolate.

The 1,1'-dinitramino-5,5'-bitetrazole represents the elegant transfer of the concept for the synthesis of 1,1'-dihydroxy-5,5'-bitetrazole to the chemistry of 1-nitraminotetrazoles. The compound unfolds the similarity of the chemistry of 1-hydroxytetrazoles and 1-nitraminotetrazoles. The major difference is that N-oxides usually make the tetrazole less sensitive whereas the nitramine on the ring causes a significant increase in sensitivity.

14. 1,1'-Dinitramino-5,5'-azobitetrazole

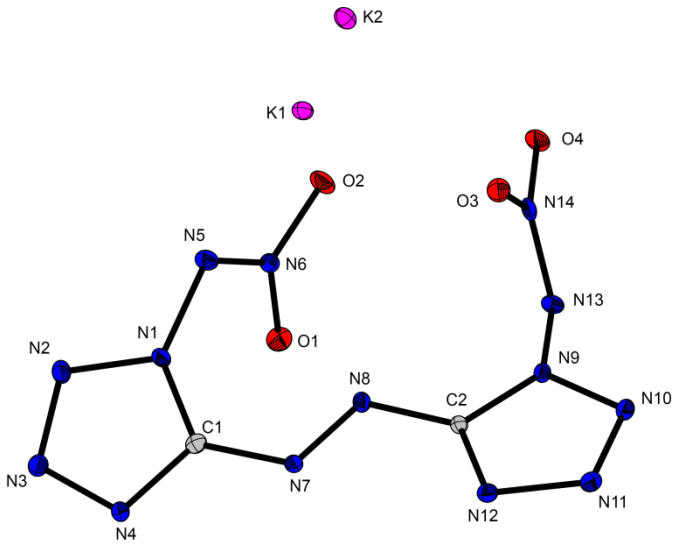


Figure 33: Crystal structure of dipotassium 1,1'-dinitramino-5,5'-azobitetrazolate.

An increase in the energy content could only be achieved via the introduction of a further equivalent of dinitrogen into the molecule. 1,1'-dinitramino-5,5'-azobitetrazole was made via the direct nitration of the recently published 1,1'-diamino-5,5'-azobitetrazole under careful conditions since 1-nitraminotetrazoles are destroyed with excess nitrating reagent (figure 34).

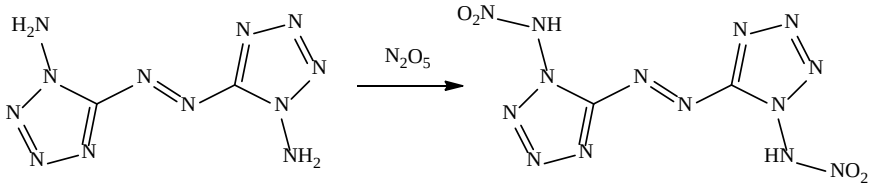


Figure 34: Synthesis of 1,1'-dinitramino-5,5'-azobitetrazole.

The dipotassium salt of this molecule is a good primary explosive too and also very sensitive but not as temperature stable as the corresponding 5,5'-bitetrazole derivative. The neutral forms of the 1,1'dinitramino-5,5'-(azo)bitetrazoles are very sensitive compounds, almost too sensitive for a normal characterization since the materials explode sometimes without external influence. The azo bridge increases the sensitivity and decreases the thermal stability of the compound further in comparison with the parent C-C connected heterocycle which is a widely applicable correlation.

15. Tetranitratoethane

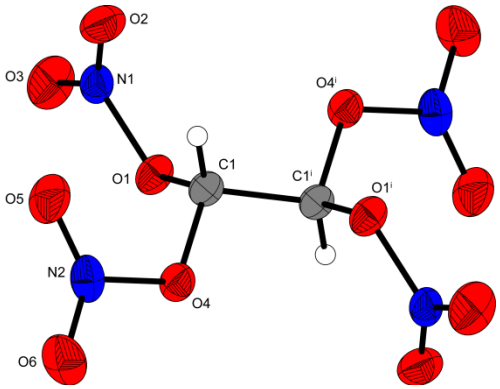


Figure 35: Crystal structure of tetranitratoethane.

The quest for high oxygen containing CHNO oxidizers lead to the discovery of the tetranitratoethane molecule. Tetranitratoethane is a gem dinitrate ester with an exceptionally high oxygen content which is obtained from the nitration of monomeric glyoxal with N_2O_5 (figure 36).

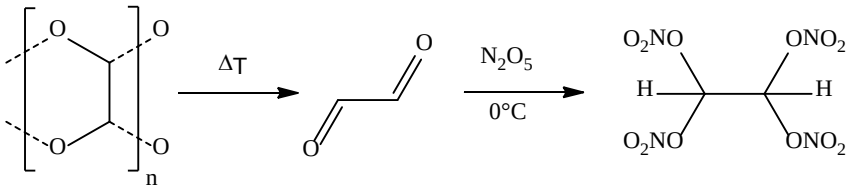


Figure 36: Synthesis of tetranitratoethane.

Tetranitratoethane is a solid state oxidizer consisting of more than 70% oxygen. It releases nitric oxides when burned in the flame. The molecule is proofing that nowadays interesting molecules with unconventional properties still can be formed in one step from simple compounds which are known for more than 100 years.

16. Copperhalotetrazolates

The work with primary explosives which do not contain any toxic metal was leading to the discovery of the laser ignitability of the copper(II)-5-halotetrazolates, which are known to be useful primaries.

17. The difluoroiodates as agent defeat ingredients

Regarding the field of agent defeat compounds it was considered to increase the disinfecting power by additionally releasing iodine in the detonation products. This lead to the investigation of the difluoroiodates as potential agent defeat ingredients. Combined with organic cations the resulting compounds release HF and I_2 upon detonation. The difluoroiodates cat^+ $IO_2F_2^-$ are simply formed from regular iodates cat^+ IO_3^- in concentrated aqueous HF solution without the need of fluorine and special equipment for its handling.

The ammonium and guanidinium difluoroiodate (figure 37) were investigated and shown to be highly efficient antiseptic explosives.

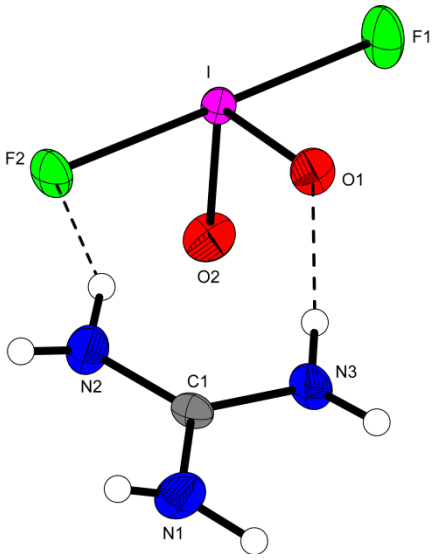


Figure 37: Crystal structure guanidinium difluoroiodate.

18. The most powerful compounds

In summary in this thesis 30 new CHNO explosives with a calculated detonation velocity over 9000 m s^{-1} were synthesized for the first time, 11 of which having a calculated detonation pressure of 400 kbar or higher. The compounds and their properties are listed in the tables below.

Table 1a: Most energetic compounds of the thesis and their properties

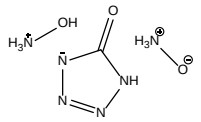
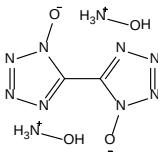
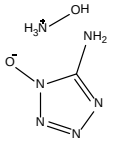
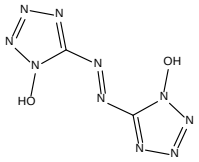
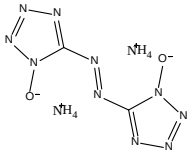
Structure					
Formula	$CH_8N_6O_3$	$C_2H_8N_{10}O_4$	$CH_6N_6O_2$	$C_2H_2N_{10}O_2$	$C_2H_8N_{12}O_2$
FW / g mol^{-1}	152.13	236.15	134.12	198.10	232.16
IS / J [a]	>40	20	10	<1	3
FS / N [b]	>360	120	>360	<5	160
ESD / J [c]	0.4	0.1	0.3	0.01	0.2
N / % [d]	55.25	59.3	62.67	70.70	72.40
Ω / % [e]	-31.55	–27.10	–35.79	–24.23	–41.34
$T_{dec.}$ / °C [f]	138	221	155	170	250
ρ / g cm^{-3} [g]	1.634	1.877	1.735	1.902	1.800
$\Delta_f H_m°$ / kJ mol^{-1} [h]	167	446.6	278.3	883.2	551.7
$\Delta_f U°$ / kJ kg^{-1} [i]	1239	2006.1	2204.3	4545.3	2493.1
EXPLO5 values:	V5.04	V5.05	V5.05	V5.05	V5.05
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	6151	6025	5984	6648	4793
T_{det} / K [k]	3716	3954	3725	4973	3313
P_{C-J} / kbar [l]	324	424	357	424	338
$V_{det.}$ / m s^{-1} [m]	9034	9698	9312	9548	9032
V_o / L kg^{-1} [n]	933	846	892	733	837

Table 1b: Most energetic compounds of the thesis and their properties

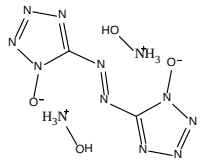
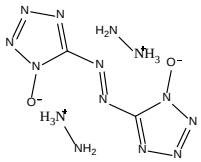
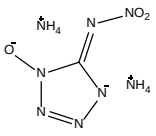
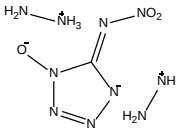
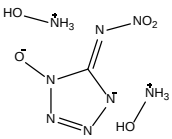
Structure					
Formula	$C_2H_8N_{12}O_4$	$C_2H_{10}N_{14}O_2$	$CH_8N_8O_3$	$CH_{10}N_{10}O_3$	$CH_8N_8O_5$
FW / g mol^{-1}	264.16	262.19	180.13	201.02	232.16
IS / J [a]	15	3	10	6	3
FS / N [b]	54	20	260	80	72
ESD / J [c]	0.2	0.7	>1.5	0.2	0.2
N / % [d]	63.63	74.79	63.21	69.66	52.82
Ω / % [e]	–24.22	–42.71	−26.6	–30.45	–7.54
$T_{dec.}$ / °C [f]	190	180	150	160	130
ρ / g cm^{-3} [g]	1.778	1.725	1.750	1.670	1.675
$\Delta_f H_m°$ / kJ mol^{-1} [h]	730.9	916.7	27.4	491.8	491.8
$\Delta_f U°$ / kJ kg^{-1} [i]	2878.7	3618.1	282.9	2475.7	2475.7
EXPLO5 values:	V5.05	V5.05	V6.03	V6.03	V6.03
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	6456	5756	4259	5999	7622
T_{det} / K [k]	4310	3711	2820	3490	3926
P_{C-J} / kbar [l]	375	350	334	366	373
$V_{det.}$ / m s^{-1} [m]	9348	9246	9475	9842	9602
V_o / L kg^{-1} [n]	841	856	996	1017	969

Table 1c: Most energetic compounds of the thesis and their properties

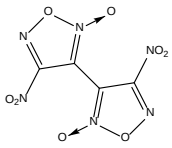
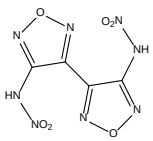
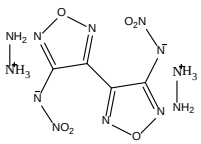
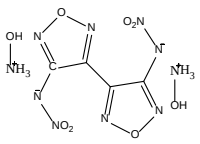
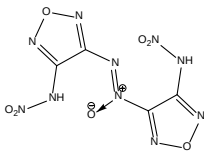
Structure					
Formula	$C_4N_6O_8$	$C_4H_2N_8O_6$	$C_4H_{10}N_{12}O_6$	$C_4H_8N_{10}O_8$	$C_4H_2N_{10}O_7$
FW / g mol^{-1}	260.08	258.11	322.20	324.17	302.12
IS / J [a]	-	1.5	6	11	1
FS / N [b]	-	48	120	288	16
ESD / J [c]	-	0.03	0.3	0.1	0.05
N / % [d]	32.31	43.41	52.17	43.21	46.36
Ω / % [e]	0	−18.59	−34.76	−19.74	−10.59
$T_{dec.}$ / °C [f]	--	80	230	141	70
ρ / g cm^{-3} [g]	1.970	1.94	1.78	1.93	1.88
$\Delta_f H_m°$ / kJ mol^{-1} [h]	448.9	526	637	417	772
$\Delta_f U°$ / kJ kg^{-1} [i]	1792	2114	2085	1384	2634
EXPLO5 values:	V6.02	V5.05	V5.05	V5.05	V5.05
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	7740	7031	6327	6612	7104
T_{det} / K [k]	5452	5291	4205	4455	5432
$P_{C\text{-}J}$ / kbar [l]	412	414	354	425	400
$V_{det.}$ / m s^{-1} [m]	9525	9255	9058	9363	9131
V_o / L kg^{-1} [n]	677	664	794	738	667

Table 1d: Most energetic compounds of the thesis and their properties

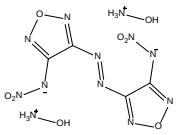
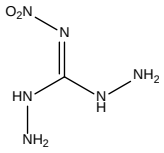
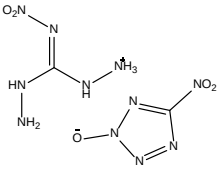
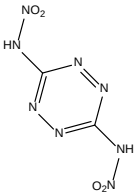
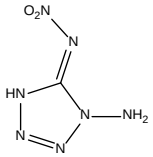
Structure					
Formula	$C_4H_8N_{12}O_8$	$CH_6N_6O_2$	$C_2H_7N_{11}O_5$	$C_2H_2N_8O_4$	$CH_3N_7O_2$
FW / g mol^{-1}	352.18	134.10	265.15	202.09	145.08
IS / J [a]	4	-	-	-	2
FS / N [b]	80	-	-	-	5
ESD / J [c]	0.13	-	-	-	1
N / % [d]	47.73	62.67	58.11	55.45	67.58
Ω / % [e]	4.73	–35.79	–15.08	–7.92	–16.54
$T_{dec.}$ / °C [f]	−18.17	136	90	120	145
ρ / g cm^{-3} [g]	150	1.735	1.766	1.909	1.777
$\Delta_f H_m°$ / kJ mol^{-1} [h]	1.85	208.0	618.6	534.1	440.6
$\Delta_f U°$ / kJ kg^{-1} [i]	718	1680.1	2440.2	2728.1	3139.0
EXPLO5 values:	V5.05	V5.04	V5.04	V5.04	V5.04
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	6911	5463	6614	6673	6221
T_{det} / K [k]	4724	3516	4559	5047	4532
$P_{C\text{-}J}$ / kbar [l]	403	341	373	419	368
$V_{det.}$ / m s^{-1} [m]	9273	9122	9211	9340	9170
V_o / L kg^{-1} [n]	748	892	817	715	807

Table 1e: Most energetic compounds of the thesis and their properties

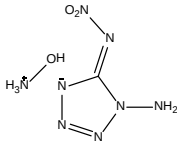
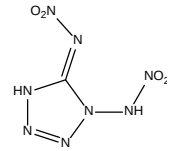
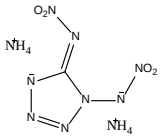
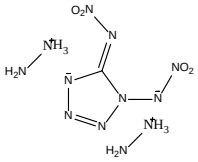
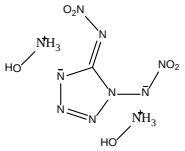
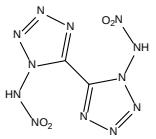
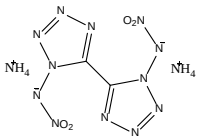
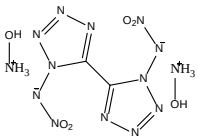
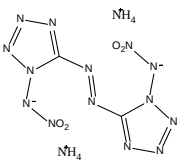
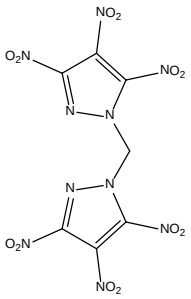
Structure					
Formula	$CH_6N_8O_3$	$CH_2N_8O_4$	$CH_8N_{10}O_4$	$CH_{10}N_{12}O_4$	$CH_8N_{10}O_6$
FW / g mol^{-1}	178.11	190.02	224.14	254.09	256.06
IS / J [a]	3	1	1.5	1	1.5
FS / N [b]	10	<5	30	6	10
ESD / J [c]	0.7	0.3	1.5	0.5	0.2
N / % [d]	62.91	58.95	62.49	68.58	54.68
Ω / % [e]	−29.61	8.42	−14.27	−18.88	0
$T_{dec.}$ / °C [f]	160	110	170	150	130
ρ / g cm^{-3} [g]	1.836	1.930	1.698	1.746	1.813
$\Delta_f H_m°$ / kJ mol^{-1} [h]	458.4	486.3	212.0	541.3	351.5
$\Delta_f U°$ / kJ kg^{-1} [i]	2691.3	2649.6	1067.4	2256.5	1488.3
EXPLO5 values:	V5.04	V6.02	V6.02	V6.02	V6.02
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	5818	5921	5240	6082	6619
T_{det} / K [k]	3801	4211	3453	3658	4158
$P_{C\text{-}J}$ / kbar [l]	398	434	315	376	399
$V_{det.}$ / m s^{-1} [m]	9589	9967	9078	9872	9807
V_o / L kg^{-1} [n]	875	836	978	1003	951

Table 1f: Most energetic compounds of the thesis and their properties

Structure					
Formula	$C_2H_2N_{12}O_4$	$C_2H_8N_{14}O_4$	$C_2H_8N_{14}O_6$	$C_2H_8N_{16}O_4$	$C_2H_8N_{14}O_6$
FW / g mol^{-1}	262.19	292.18	324.18	201.02	418.15
IS / J [a]	< 1	2	2	< 1	4
FS / N [b]	< 5	< 5	5	< 5	144
ESD / J [c]	0.03	0.2	0.1	0.05	0.1
N / % [d]	65.12	67.11	60.49	69.99	33.50
Ω / % [e]	–6.20	−21.90	−9.87	−19.96	−11.48
$T_{dec.}$ / °C [f]	107	210	155	170	205
ρ / g cm^{-3} [g]	1.968	1.848	1.842	1.753	1.934
$\Delta_f H_m°$ / kJ mol^{-1} [h]	932.1	647.7	789.8	941.9	378.6
$\Delta_f U°$ / kJ kg^{-1} [i]	3697.1	2327.0	2543.3	3050.0	976.8
EXPLO5 values:	V6.03	V6.03	V6.03	V6.03	V6.02
$-\Delta_{Ex}H°$ / kJ kg^{-1} [j]	6629	5325	6384	5752	6254
T_{det} / K [k]	4645	3536	4083	3843	4570
$P_{C\text{-}J}$ / kbar [l]	456	361	418	358	393
$V_{det.}$ / m s^{-1} [m]	10142	9519	9885	9472	9300
V_o / L kg^{-1} [n]	808	908	879	908	704

[a] impact sensitivity, BAM drophammer (method 1 of 6); [b] friction sensitivity, BAM friction tester (method 1 of 6); [c] electrostatic discharge device (OZM research); [d] nitrogen content; [e] oxygen balance calculated for N_2, H_2O and CO_2; [f] temperature of decomposition according to DSC (onset temperatures at heating rates of 5 deg min^{-1}); [g] X-ray densities; [h] heat of formation; [i] energy of formation; [j] heat of detonation; [k] detonation temperature; [l] detonation pressure; [m] detonation velocity; [n] volume of gases after detonation.

From the chemical point of view the major merit of this thesis is the synthesis of new highly energetic and nitrogen-rich covalent compounds and ionic derivatives thereof. The search for useful and yet unknown HEDMs and the development of simple strategies for their synthesis is a difficult and time consuming business requiring a broad knowledge about the existing HEDMs and their synthesis paths.

19. The most useful compounds

In terms of practical applicability the best compounds of this thesis are

1. TKX-50 as a secondary explosive because it fulfills most of the requirements for a modern RDX-replacement. They state that the explosive power should be equal or at least higher than RDX, the sensitivities should be lower and the thermal stability should be at least 200°C.
2. K_2DNABT as a heavy metal free pimary explosive because of its high initiation power and the thermal stability of over 200°C.
3. K_2DNAT as ingredient in priming mixtures because of its good initiation ability and its high decomposition temperature of 240°C.
4. OHN as explosive or ingredient of smokeless propellants because of its high thermal stability, its smokeless combustion and its simple and cost effective preparation.
5. BDNAPM combines high temperature stability (T_{DEC} = 310 °C) and low sensitivity (IS 11 J, FS > 360 N) with acceptable explosive performance ($p_{C\text{-}J}$ = 295 kbar, D = 8372 m s^{-1}). Because of its favourable crystal shape the material can be pressed into dense charges.
6. BTNPM is an oxygen-rich explosive with the power equal to HMX. The material is stable up to 200 °C and can be used in aluminized formulations.

The results of this thesis confirm the former known principles of powerful explosives. The question is how far the game towards more powerful but still applicable CHNO explosives can be driven. The N-nitraminotetrazoles show that highly endothermic and nitrogen-rich compounds tend to be also highly sensitive. The density seems to be the parameter of choice for the development of new high performing explosives but it has to be considered that the power improvements are in the region of 10% or less whereas the synthetical efforts are growing disproportional.

APPENDIX

The following appendix contains a list of manuscripts, which were published within the scope of this dissertation. These manuscripts have been published in peer-reviewed journals and are subject to copyrights, therefore they have been reproduced with permission of the corresponding publisher. Furthermore a published patent application, an invention disclosure and a Curriculum Vitae as well as a bibliography are attached. The publications are listed chronologically according to the year of publication without changing the format of the respective scientific journal. Supporting information of the respective publications is not printed here but available via the web pages of the publishers. If additional information is published in the internet a link for “supporting information” or “supplementary information” is given in the articles.

ARTICLE

DOI: 10.1002/zaac.201100052

Synthesis and Characterization of Guanidinium Difluoroiodate, $[C(NH_2)_3]^+[IF_2O_2]^-$ and its Evaluation as an Ingredient in Agent Defeat Weapons[‡]

Dennis Fischer,[a] Thomas M. Klapötke,*[a] and Jörg Stierstorfer[a]

Dedicated to Prof. Peter Klüfers on the occasion of his 60th birthday

Keywords: Agent Defeat Weapons (ADW); Diazidoglyoxime; Difluoroiodate; Explosives; Geobacillus Stearothermophilus; X-ray diffraction

Abstract. Ammonium and guanidinium difluoroiodate(V), $[NH_4]^+[IF_2O_2]^-$ (**1a**) and $[C(NH_2)_3]^+[IF_2O_2]^-$ (**1b**), and diazidoglyoxime, $[N_3C{=}N{-}OH]_2$ (**2**) were synthesized and the molecular structures in the solid state of **1b** and **2** were elucidated by single-crystal X-ray diffraction. **1b**: $P\bar{1}$, a = 6.6890(5), b = 10.2880(6), c = 10.30.92(8) Å, α = 105.447(6), β = 108.568(7), γ = 91.051(5)°, V = 644.08(8) Å^3, ρ = 2.650 g·cm^{-3}; **2**: $P2_1/n$, a = 4.4211(3), b = 13.7797(9), c = 4.9750(3) Å, β = 98.735(6), V = 299.57(3) Å^3, ρ = 1.886 g·cm^{-3}. The suitability of compounds **1a** and **1b** as active ingredients for agent defeat weapons (ADW) with biocidal activity has been shown in detonation tests using geobacillus stearothermophilus spores. In addition, a complete energetic characterization of the promising primary explosive **2** is given.

Introduction

Operation Desert Storm highlighted the need for pre-emptive strike capability to disable chemical and biological (CB) agent munition production facilities and stockpiles. The Agent Defeat Warhead (ADW) Demonstration (ADWD) program objective is to develop and demonstrate a warhead with a payload specifically tailored for use against fixed ground targets associated with the development, production, and storage of chemical (C) agents, biological (B) agents, and CB weapons (CBW).[1]

Agent Defeat Weapons (also known as agent defeat warheads, ADW) are airborne warheads, which can be used in the fight against chemical and biological (CB) weapons of mass destruction (WMD) to minimize the amount of collateral damage that occurs. Such collateral damages can be largely minimized when the active agents in the chemical or biological weapons are destroyed or neutralized upon being attacked, before they can be spread into the environment.[1] Most ADWs are thermobaric weapons and use incendiary chemical fills (e.g. Ti/B/Li perchlorate) in order to generate heat and long lasting fires. In addition, some ADWs also contain chlorine-releasing systems, which also provide further destruction through oxidation in particular of the biological warfare agents. Other chemical compounds, which are suitable for fighting biological agents may contain fluorine-containing compounds, peroxides or hypochlorites.[1] It has been shown[2] that although Cl_2 is a better biocide than HCl, the biocidal activity of HF exceeds both Cl_2 and HCl. 200 ppm HF destroy most bacteria, including Anthrax spores.[2] Two active HF-generating ingredients suggested by *Chapman* include octa-F-PETN, $C(CH_2{-}NF_2)_4$, and HNFX-1, $[N(NO_2){-}CH_2{-}C(NF_2)_2{-}CH_2]_2$. Although these ingredients respective their detonation products show strong biocidal activity, the two disadvantages are that they (i) require sophisticated synthetic procedures for their preparation and (ii) do not provide any extra oxygen, which is needed for the thermobaric system. In this publication we present for the first time two fluorine- *and* iodine-containing compounds (HF and I_2 are both strong biocides), which have a positive oxygen balance, namely ammonium and guanidinium difluoroiodate, $[NH_4]^+[IF_2O_2]^-$ (**1a**)[3,4] and $[C(NH_2)_3]^+[IF_2O_2]^-$ (**1b**). Compounds **1a** and **1b** were formulated with the powerful primary explosive diazidoglyoxime, $[N_3C{=}N{-}OH]_2$ (**2**)[5] in order to obtain an explosive formulation with an oxygen balance of essential zero.

* Prof. Dr. T. M. Klapötke
Fax: +49-89-2180-77492
E-Mail: tmk@cup.uni-muenchen.de
[a] Ludwig Maximilian University Munich (LMU)
Department of Chemistry
Energetic Materials Research
Butenandtstr. 5–13 (D)
81377 Munich, Germany

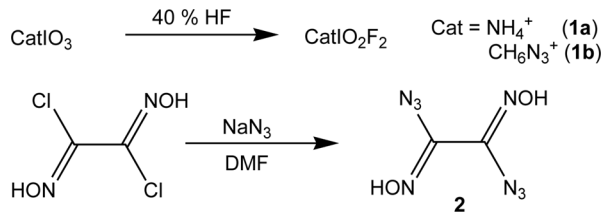
[‡] This paper has been presented in part as an oral presentation (FLUO 44) at the 20th Winter Fluorine Conference of the American Chemical Society, St. Pete Beach, Fl., January 9-14, 2011.

Results and Discussion

Synthesis

According to the literature procedure,[6] ammonium and guanidinium difluoroiodate were synthesized by dissolving the

corresponding iodates in 40 % HF. After a few days crystals of the difluoroiodates **1a** and **1b** appeared and were collected and kept under dry diethyl ether. Diazidoglyoxime (**2**) was synthesized by displacing the chloride in dichloroglyoxime[7] with sodium azide in DMF (Scheme 1). The colorless product could be isolated in good yields by filtration after pouring the suspension into water.[8]



Scheme 1. Synthesis of difluoroiodates **1a** and **1b** and diazidoglyoxime **2**.

Crystal Structures

To determine the molecular structures of **1b** and **2** in the crystalline state an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a Kappa CCD detector was used. The data collection was performed using the CrysAlis CCD software,[9] the data reductions with the CrysAlis RED software.[10] The solution and refinement of all structures were performed using the programs SIR-92,[11] SHELXS-97,[12] and SHELXL-97[13] implemented in the WinGX software package[14] and finally checked with the PLATON software.[15] In the crystal structures the hydrogen atoms were located and refined. The absorptions were corrected with the SCALE3 ABSPACK multi-scan method.[16] Selected data and parameter of the X-ray determinations are given in Table 1.

Guanidinium difluoroiodate crystallizes in the triclinic space group $P\bar{1}$ with four cation/anion pairs in the unit cell. The

Table 1. X-ray data and parameters.

	1b	**2**
Formula	$CH_6N_3F_2IO_2$	$C_2H_2N_8O_2$
Form. weight /g·mol^{-1}	256.99	170.12
Crystal system	Triclinic	Monoclinic
Space Group	$P\bar{1}$ (2)	$P2_1/n$ (14)
Color / Habit	Colorless rod	Colorless rod
Size /mm	0.14 × 0.16 × 0.21	0.10 × 0.20 × 0.30
a /Å	6.6890(5)	4.4211(3)
b /Å	10.2880(6)	13.7797(9)
c /Å	10.3092(8)	4.9750(3)
α /°	105.447(6)	90
β/°	108.568(7)	98.735(6)
γ /°	91.051(5)	90
V /pm^3	644.08(9)	299.57(3)
Z	4	2
$\rho_{calcd.}$ /g·cm^{-3}	2.650	1.886
μ /mm^{-1}	4.951	0.164
F(000)	480	172
λ (Mo-K_α) /Å	0.71073	0.71073
T /K	100	173
θ min–max /°	4.3, 26.0	4.4, 26.1
Dataset	–8:8	–4:5
	–12:12	–17:16
	–12:12	–5:6
Reflections collected	5011	1545
Independent reflections	2502	595
R_{int}	0.032	0.019
Observed reflections	1972	464
Parameters	211	59
R_1 (obs)	0.0235	0.0277
wR_2 (all data)	0.0486	0.0665
S	0.90	0.98
Resd. Dens. /e·Å^{-3}	–0.60, 0.67	–0.17, 0.17
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	multi-scan	multi-scan
CCDC	808234	808233

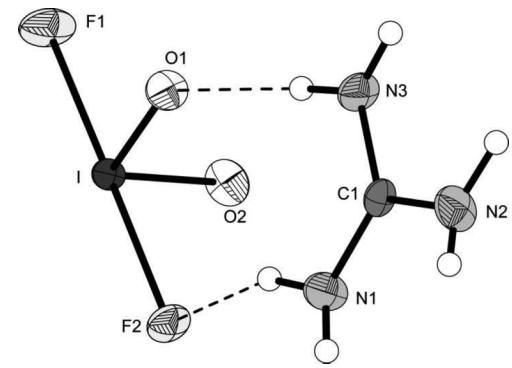


Figure 1. Molecular moiety of guanidinium difluoroiodate (**1b**). Ellipsoids represent 50 % probability. Selected bond lengths /Å: I–F1 1.976(3), I–F2 2.030(2), I–O1 1.765(3), I–O2 1.768(4), N1–C1 1.323(6), N2–C1 1.319(7), N3–C1 1.319(7); selected bond angles /°: O1–I–O2 104.23(16), F1–I–O2 91.80(15), F1–I–F2 177.98(12), F1–I–O1 89.70(13), F2–I–O1 89.01(13), N1–C1–N3 119.1(5), N1–C1–N2 120.6(5), N2–C1–N3 120.4(5).

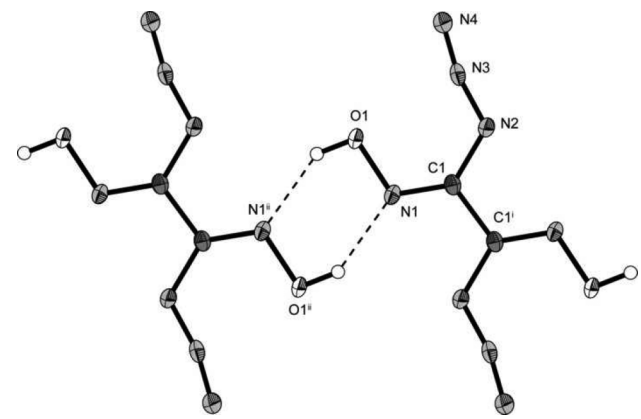


Figure 2. View on the hydrogen bonds in the structure of diazidoglyoxime (**2**) showing two molecular moieties. Ellipsoids represent the 50 % probability level. (i) 1–x, 1–y, 1–z (ii) 2–x, 1–y, 2–z. Selected bond lengths /Å: O1–N1 1.3959(14), N1–C1 1.2798(15), N3–N4 1.1237(15), N3–N2 1.2559(15), N2–C1 1.3991(17), C1–C1^i 1.474(2); selected bond angles /°: C1–N1–O1 113.46(11), N4–N3–N2 167.39(13), N3–N2–C1 119.53(11), N1–C1–N2 130.57(12), N1–C1–C1^i 116.62(14), N2–C1–C1^i 112.80(13); selected torsion angles (°): N3–N2–C1–C1^i 172.43(13), O1–N1–C1–C1 179.92(13).

structure of the difluoroiodate anion follows that of sodium difluoroiodate[17] and potassium difluoroiodate[18] in the literature. The guanidinium anion has a planar structure and is in agreement to other guanidinium salts, e.g. guanidinium 1-methyl-5-nitriminotetrazolate.[19] The packing is strongly dominated by a 3-dim network, in which all of the guanidinium hydrogen atoms participate in hydrogen-bonds (Figure 1).

Crystals of diazidoglyoxime (**2**) suitable for X-ray analysis were obtained from ethanol. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell. Two molecular moieties are shown in Figure 2. The constitution of the azide group is similar to those of other covalent carbon bonded azide groups, e.g. in azidoformamidinium chloride.[20] The azide group is angulated (N5–N6–N7 = 167.4(1)°), which is quite common for covalent azides and can be explained by hyperconjugation effects.[21] The high density of 1.886 g·cm^{-3} can be explained by the formation of hydrogen bonds as shown in Figure 2. The oximes form six membered rings consisting of two identical hydrogen bonds. This hydrogen bonds lead to the formation of chains in the structure of **2**.

Biocidal Activity

Figure 3 summarizes the experimentally observed colony count (see also Table 4) for four detonation experiments using the following notations:

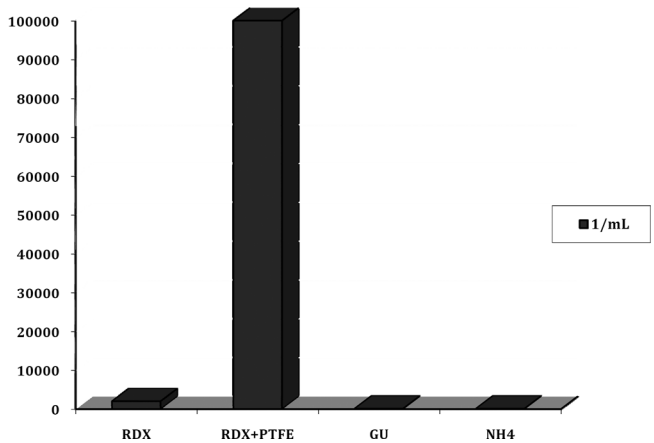


Figure 3. Number of colonies counted.

Table 4. Colony count after 48 hrs at 40 °C.

	colonies /mL	reduction of spore activity
blank sample	2.2×10^8	–
RDX	2.0×10^3	2×10^5
$[NH_4]^+[IF_2O_2]^-$	< 100	> 2.2×10^7
$[C(NH_2)_3]^+[IF_2O_2]^-$	< 100	> 2.2×10^7

- RDX = 100 mg RDX + 75 mg diazidoglyoxime
- RDX + PTFE = 50 mg RDX + 50 mg PTFE + 75 mg diazidoglyoxime
- GU = 100 mg $[C(NH_2)_3]^+[IF_2O_2]^-$ + 75 mg diazidoglyoxime
- NH4 = 100 mg $[NH_4]^+[IF_2O_2]^-$ + 75 mg diazidoglyoxime

Whereas RDX alone reduces the bacterial count already by a factor of 2×10^5, a RDX/PTFE mixture only reduces the growth by a factor of 2×10^3. This finding can best be explained by the biocidal activity of exploding RDX due to its shock-wave and heat, which is less intense when the RDX is "diluted" with 50 % PTFE. The fact that PTFE does not form significant amounts of biocidal HF agrees with *Chapman*'s findings that HF is best generated from $–NF_2$ rather than from $–CF_3$ groups. The latter observation can be further explained by the higher bond energy of the C–F (117 kcal·mol^{-1})[22] vs. the N–F bond (66.4 kcal·mol^{-1})[22] and the preferred formation of COF_2 (rather than HF) in explosions involving $–CF_3$ groups.

The two difluoroiodate containing formulations on the other hand show an even stronger bacterial growth inhibition (2.2×10^6) than pure RDX (2×10^5) (Figure 4) and indicate that the difluoroiodate anions contribute strongly to the biocidal activity of the formulations used.

In order to theoretically analyze the detonation products formed we calculated the composition of the reaction products using the ICT code[23] for an ADW formulation consisting of ammonium difluoroiodate and diazidoglyoxime (4:3, w/w)

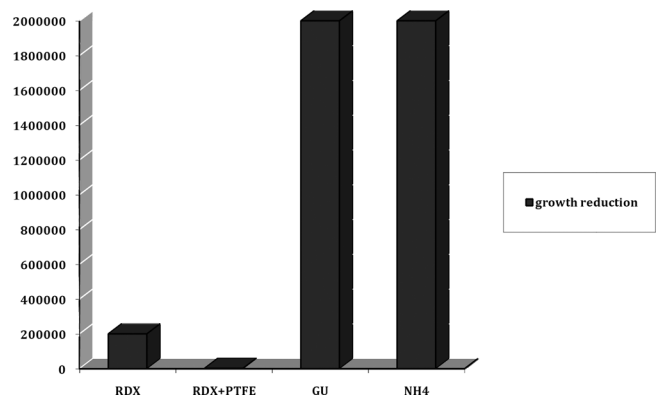


Figure 4. Inhibition of bacteria growth.

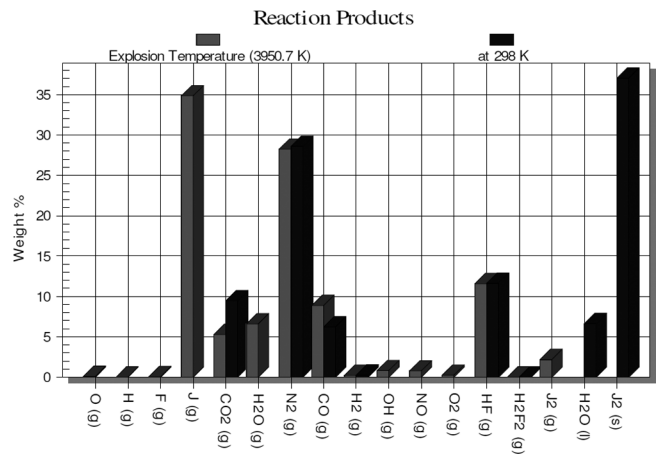


Figure 5. Detonation products (in wt.-%) for a 4:3 (w/w) mixture of ammonium difluoroiodate and diazidoglyoxime.

Table 2. Heat of formation calculation of diazidoglyoxime (**2**).

	$-H^{298}$ /a.u.	$\Delta_fH°$(g,M) /kcal·mol^{-1}	$T_{dec.}$ /°C	$\Delta_fH°$(s) /kcal·mol^{-1}	$\Delta_fH°$(s) /kJ·mol^{-1}	Δn	M /g·mol^{-1}	$\Delta_fU°$(s) /kJ·kg^{-1}
2	664.785302	184.3	170	164.4	688.3	–6	170.12	4133.5

Table 3. Energetic Properties of **2**.

	IS /J	FS /N	ESD /J	N /%	Ω /%	Density /g·cm^{-3}	$-\Delta_EU°$ /kJ·kg^{-1}	p_{C-J} /kbar	D /m·s^{-1}
2	1.5	5	0.007	65.88	28.22	1.886	6580	407	9382

(Figure 5 and Figure 6). Figure 5 and Figure 6 show the composition in weight-% and in mol-% of the explosion products for an explosion temperature of 3950 K (grey) and for equilibrium conditions at room temperature (black). Both figures clearly show that essentially all fluorine gets converted into biocidally active HF (both at 3950 K and 298 K) and that all iodine transforms into I (3950 K) and I_2 (298 K), which are strong biocides as well. Moreover, the calculated oxygen balance of this mixture of Ω = –3.5 % shows an essentially balanced oxidizer/fuel ratio, which could easily be changed to a positive value (overoxidized) simply by increasing the iodate:diazidoglyoxime ratio.

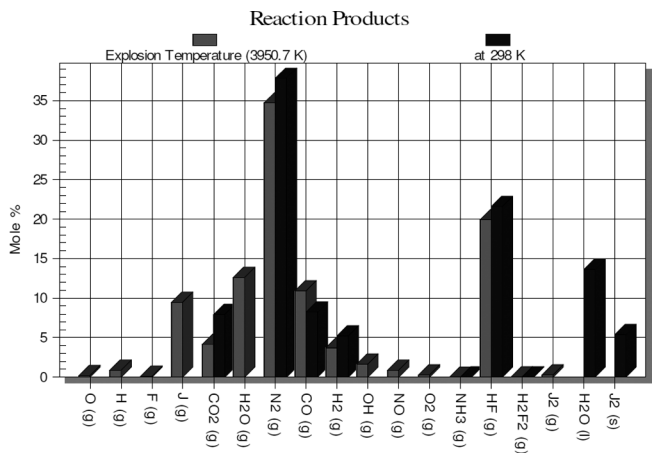


Figure 6. Detonation products (in mol-%) for a 4:3 (w/w) mixture of ammonium difluoroiodate and diazidoglyoxime.

Energetic Properties

Heat of formation calculation of compound **2** was performed using the atomization method based on CBS-4M enthalpies described recently in detail in the literature.[24] The quantum chemical calculation was performed with the Gaussian09 software.[25] The results are depicted in Table 2 and Table 3. The gas phase heat of formation ($\Delta_fH°$(g,M)) was converted into the solid state heat of formation ($\Delta_fH°$(s)) using *Trouton*'s rule.[26]

The sensitivities of compounds **1a**, **1b** and **2** were determined using the BAM drophammer and friction tester[27] as well as an OZM small scale electrostatic discharge device[28] following standard protocols described in the references of literature.[24] Compounds **1a** and **1b** decomposed during the determination of their impact sensitivities at values of 5 and 4 J, respectively. It was not possible to determine the exact values using the BAM setup because the difluoroiodates reacted with steel rollers, however no explosion occurred on both **1a** and **1b** up to 40 J impact. Friction sensitivities of **1a** and **1b** were determined to be 360 N and > 288 N, respectively, whereas only decomposition occurred. With an ESD sensitivity of about 1 J, compounds **1a** and **1b** are quite insensitive materials. According to the UN recommendations of the transport of dangerous goods,[29] **2** is very sensitive towards impact and friction. Compound **2** strongly fulminates when it is hold into a flame. Using the high calculated heat of formation of 688.3 kJ·mol^{-1} and its crystal density of 1.886 g·cm^{-3}, several detonation parameters were computed with the EXPLO5.04 code.[30] It shows a superior calculated detonation velocity of 9382 m·s^{-1} and a detonation pressure of 407 kbar, which are higher values than those calculated for RDX (8748 m·s^{-1} and 349 kbar). The sensitivities, in combination with its rapid deflagration to detonation transition and the high calculated performance make diazidoglyoxime a promising metal free primary explosive.

Conclusions

From this study the following conclusions can be drawn:

(i) C–F groups, e.g. $–CF_2–CF_2–$ (PTFE) are not good as a source for HF in ADWs.

(ii) The introduction of fluorine via a non-explosive compound in ADWs is possible in the form of difluoroiodate salts.

(iii) No $–NF_2$ groups are needed in order to generate HF during the explosion of the ADW.

(iv) Iodine (I and I_2) in addition to HF is a "good" bactericide for the use in ADWs.

(v) The system: diazidoglyoxime / (ammonium or guanidinium) difluoroiodate shows bactericidal growth reduction > 2.2×10^6.

(vi) Both ingredients are easily available (cheap and easy synthesis).

(vii) The crystal structures of guanidinium difluoroiodate(V) (**1b**) and diazidoglyoxime (**2**) were determined and discussed.

(viii) The energetic properties of **2** were investigated experimentally and theoretically. Due to the high sensitivities (IS 1.5 J, FS 5 N) and great performance **2** can be used as a metal free primary explosive.

Experimental Section

All explosive formulations consisted of 75 mg diazidoglyoxime (explosive) and 100 mg agent defeat ingredient: 100 mg RDX (reference without fluorine and iodine), 50 mg RDX + 50 mg PTFE (PTFE as potential fluorine source); $[NH_4]^+[IF_2O_2]^-$, $[C(NH_2)_3]^+[IF_2O_2]^-$. The formulation was placed in a plastic tube (diameter 5 mm, length 5 cm) and initiated with an electrical match.

A standardized spore suspension (2 mL, MERCK, No. 1.11499.0001) of geobacillus stearothermophilus (2.2×10^8 spores·mL^{-1}) was loaded in a hermetically sealed 2 L polyethylene (PE) lined detonation bomb in the center of which the above described plastic tube containing the agent defeat formulation was detonated. Immediately after detonation (within 5 min) the contents of the PE lined bomb was rinsed out and incubated for 72 hrs at 55 °C using an Agar-based medium (Merck, No.1.07881.0500). The numbers of colonies counted are summarized in Table 4.

Hexogen (RDX): Synthesized analog to a literature described procedure.[31] Urotropine (12.0 g, 86 mmol) was dissolved in 100 % nitric acid (90 mL, 2.2 mol) at 20 °C. The solution was stirred for 40 min at room temperature and was afterwards added in small portions to a mixture of sodium nitrite (1.23 g, 18 mmol) and 65 % nitric acid (6 mL) while the temperature was kept between 50 °C and 70 °C. After addition, the mixture was kept for further 40 min at 70 °C and was afterwards cooled to 5 °C and poured into crushed ice (300 mL). The precipitate was filtered, washed with water (120 mL) and dried yielding 15.6 g (82 %) of a colorless and crystalline solid. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 6.06; **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 61.7; **EA** ($C_3H_6N_6O_6$, 222.12): calcd.: C 16.22, H 2.72, N 37.84 %; found: C 16.49, H 2.81, N 37.55 %.

Ammonium difluoroiodate: According to literature[6] ammonium iodate (1.93 g, 10 mmol) was dissolved in 40 % HF (10 mL). After being left in the fume hood for two days a crystalline solid appeared. The solid was filtered and kept under diethyl ether. **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 813 (100), 794 (86), 485 (14), 352 (15), 320 (19) cm^{-1}.

Guanidinium difluoroiodate: Guanidinium iodate (2.35 g, 10 mmol) was dissolved in 40 % HF (10 mL). After being left in the fume hood for two days a crystalline solid appeared. The solid was filtered and kept under diethyl ether. **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1017 (71), 848 (83), 838 (60), 819 (100), 539 (7), 521 (5), 465 (14), 398 (10), 359 (10), 342 (18), 333 (18), 306 (18), 293 (13) cm^{-1}.

Diazidoglyoxime: Synthesized according to a modified procedure described in the literature.[8] Dichloroglyoxime[7] (784 mg, 5 mmol) was dissolved in dimethylformamide (10 mL). At 0 °C sodium azide (841 mg, 12.93 mmol) was added. The suspension was stirred for 20 min at 0 °C and water (100 mL) was added. The precipitate was filtered, washed with water (20 mL) and air dried yielding 713 mg (84 %) of colorless product **2**. **DSC** (5 °C· min^{-1}): 170 °C (dec.). **IR** (atr): $\tilde{\nu}$ = 3209 (w), 2170 (w), 2123 (w), 1622 (w), 1400 (w), 1361 (w), 1286 (m), 1013 (vs), 930 (m), 920 (s), 855 (s), 731 (s) cm^{-1}; **Raman** (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 2166 (8), 2129 (5), 2091 (3), 1621 (100), 1457 (14), 1390 (12), 1216 (19), 1034 (3), 882 (20), 672 (3), 442 (6) cm^{-1}. **^{1}H NMR** ([D$_6$]DMSO, 25 °C): δ = 12.08; **^{13}C{^{1}H} NMR** ([D$_6$]DMSO, 25 °C): δ = 136.5; **EA** ($C_2H_2N_8O_2$, 170.09): calcd.: C 14.12, H 1.19, N 65.88 %; found: C 14.38, H 1.46, N 66.01 %; **BAM drophammer**: 1.5 J; **friction tester**: <5 N; **ESD**: 7 mJ.

Acknowledgement

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Copper Salts of Halo Tetrazoles: Laser-Ignitable Primary Explosives

DENNIS FISCHER,[1] THOMAS M. KLAPÖTKE,[1,2] DAVIN G. PIERCEY,[1] and JÖRG STIERSTORFER[1]

[1]Department of Chemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich, Munich, Germany
[2]Department of Mechanical Engineering, Center for Energetic Concepts Development, University of Maryland, College Park, Maryland

Syntheses of the primary explosives copper (II) 5-chlorotetrazolate and copper (II) bromotetrazolate are described. The physical and thermal stabilities of both compounds were determined, and their explosive ability was characterized. Additionally, the first reported X-ray structure of a 5-chlorotetrazole is reported.

Keywords: laser ignition, primer, sensitivity, tetrazole

Dedicated to Professor Peter Klüfers on the occasion of his 60th birthday.

Address correspondence to Thomas M. Klapötke, Department of Chemistry, Energetic Materials Research, Ludwig-Maximilian University of Munich, Butenandstr. 5-13, D-81377 Munich, Germany. E-mail: tmk@cup.uni-muenchen.de

Introduction

Primary explosives are the highly sensitive explosives that upon ignition undergo a deflagration-to-detonation transition (DDT), generating a shockwave capable of initiating detonation in a secondary explosive. Though secondary explosives are well known and common, with dozens of examples having found extensive practical use, primary explosives are less numerous due the uniqueness of the materials that can undergo a DDT. In the initial stages of the deflagration of a primary explosive, propagation of the combustion wave is entirely thermal, and grains of primary explosives combust from the outside inwards. The pressure released during this combustion is thought to compress unreacted primary explosives ahead of the combustion front while simultaneously heating it via compression and friction to temperatures above its decomposition point, leading to the propagation of a detonation wave [1]. The relative rarity of such a process means that very few materials are suitable for use as primary explosives.

The first primary initiating explosive that found widespread use was mercury fulminate, the use of which was pioneered by Nobel [2], prior to which common black powder (75% KNO_3, 15% C, 10% S_8) was used to initiate secondary explosives in a very unreliable fashion [3]. During the last century the use of mercury fulminate has been supplanted by the more powerful and less toxic lead azide, the use of which continues to the present day. Though many other initiating primaries have been used on smaller scales, lead azide remains the current primary of choice despite possessing extensive drawbacks.

Beyond the unacceptable personal and environmental toxicity of lead [4], lead azide is also highly sensitive in the pure state, requiring dextrination to reduce sensitivity [5]. Lead azide also needs protection from carbon dioxide or decomposition ensues [6], can detonate during synthesis if conditions are not rigorously controlled [7] (lead azide is not manufactured in the United States for this reason [8]), and requires

a relatively large mass of material in order to initiate a secondary (relative to very vigorous initiators such as silver nitrotetrazolate: 5 mg vs. 20 mg for tetryl initiation) [5].

A lead azide replacement needs to possess the following properties: (1) insensitivity to light; (2) sensitivity to detonation but not too sensitive to handle and transport; (3) stable to at least 200°C; (4) stable upon storage for long periods of time; (5) free of toxic metals; (6) free of toxic perchlorate [9]. Compounds including diazodinitrophenol (DDNP) [10], 3,6-diazido-1,2,4,5-tetrazine [11], 1,3,5-triazido-2,4,6-trinitrobenzene (TATNB) [12] or tetraamine bis(nitrotetrazolato-N^2)cobalt (III) perchlorate [13], and complex nitrotetrazole primaries [9,14] have all been considered as lead azide replacements; however, their instability to light, heat, mechanical stimuli, or toxic perchlorate content preclude this use. Additionally, the use of nitrotetrazolate ions or ligands in primary explosives can be hazardous due to the synthesis of nitrotetrazole involving a very sensitive intermediate product [15].

Laser ignitability in a primary explosive offers a distinct advantage over simple electrical ignition (whether hot wire, slapper, or exploding bridge wire [EBW]) for the distance-separated ignition of blasting caps. In all detonating systems based on electric signal transmission over great distances, exceedingly long wires and cables are used. Unfortunately, the length of such conductors allows ambient electromagnetic fields to induce currents in the electrical conductor, increasing the possibility of the generation of an accidental detonation signal from electromagnetic field generators such as lightning, radio transmitters, or microwaves. The use of optical fibers instead of wires for the transmission of the detonation signal offers a distinct increase in the safety of an initiation system. Naturally, to use such optical fibers, a laser-sensitive primary explosive must be used [16].

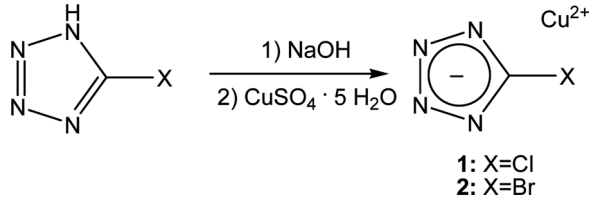
The low toxicity of copper and the known photosensitivity of energetic copper salts and complexes led us to investigate the use of copper (II) chlorotetrazolate (**1**) and copper (II) bromotetrazolate (**2**) as laser-ignitable primary explosives.

Results and Discussion

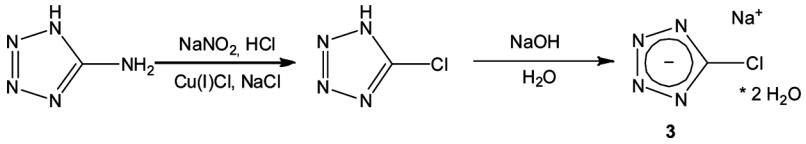
The reaction of copper (II) sulfate pentahydrate with the sodium salt of 5-chloro or 5-bromotetrazole in aqueous solution led to the instantaneous precipitation of the copper (II) chlorotetrazolate (**1**) or copper (II) bromotetrazolate (**2**) as a very fine precipitate (Scheme 1). Attempts at filtration of the halotetrazolates proved that the particle size is too small for conventional filter paper or 450-nm cellulose acetate filters, so isolation was achieved by centrifugation of the reaction mixture. Both **1** and **2** were isolated in almost quantitative yield.

5-Chloro-2*H*-tetrazole is formed by the reaction of 5-aminotetrazole with sodium nitrite, a mixture of Cu(I)Cl and NaCl in diluted hydrochloric acid (Scheme 2). A basic workup using sodium hydroxide yielded sodium 5-chlorotetrazolate dihydrate (**3**). Acidification and extraction into ethyl acetate yielded free chlorotetrazole after evaporation. An analogous procedure was used for the preparation of the bromotetrazole.

Single crystals of **3** were grown from a water: ethanol mixture. The crystals were analyzed by low-temperature X-ray diffraction on an Oxford Xcalibur3 diffractometer using a Spellman generator (voltage 50 kV, current 40 mA) and a



Scheme 1. Synthesis of copper halotetrazolates (**1** and **2**).



Scheme 2. Synthesis of sodium 5-chlorotetrazolate dihydrate (**3**).

KappaCCD detector. A suitable single crystal was picked from the crystallization mixture and mounted in Kel-F oil on a glass fiber on the goniometer head, which was transferred to the N_2 stream (200 K) of the diffractometer (Agolent Technologies). Data collection was undertaken using CrysAlis CCD software [17] and data reduction was performed with CrysAlis RED software [18]. The structure was solved with SIR-97 [19]. The data set was refined with SHELXL-97 [20] implemented in the program package WinGX [21] and finally checked using the Platon software [22]. Structural data and X-ray parameters are summarized in Table 1.

The present structure represents the first containing the 5-chlorotetrazole moiety. Sodium 5-chlorotetrazolate dihydrate (**3**) crystallizes as a dihydrate in the orthorhombic space group *Pnma* with four molecular formula in the unit cell and a density of 1.830 g cm^{-3}. The extended structure is similar to that seen for sodium tetrazolate [23]. The sodium cations have a distorted octahedral coordination sphere, which is shown in Fig. 1. Due to this coordination mode, chains are formed along the *a* axis (Fig. 2).

Compounds **1** and **2** underwent thermal and explosive sensitivity tests. The thermal stability of each (∼1 mg) was investigated by differential scanning calorimetry using a Linseis PT10 (Linseis Messgeräte GmbH, Germany) differential scanning calorimeter (DSC) at a heating rate of 5°C min^{-1}. Compound **1** exhibited superior thermal stability with an onset of exothermic decomposition beginning at 275°C and a peak exotherm at 300°C. Compound **2** possessed a slightly lower onset of exothermic decomposition beginning at 265°C and a peak exotherm at 292°C. The DSC traces of both are given in Fig. 3. The decomposition of each was also observed in a standard melting point apparatus (heating rate 5°C min^{-1}) whereby darkening of the blue materials occurred at 278 and 269°C for **1** and **2**, respectively. By 300 or 285°C for **1** and **2** the samples had either detonated or turned black (CuO formation) during the multiple trials performed.

For initial safety testing, the impact, friction, and electrostatic discharge sensitivities were determined [24]. The impact sensitivity tests were carried out according to STANAG 4489

Table 1
X-ray diffraction data and parameters

	3		**3**
Formula	$CH_4ClN_4NaO_2$	Independent reflection	631
Form. weight (g mol^{-1})	162.52	R_{int}	0.033
Crystal system	Orthorhombic	Observed reflection	586
Space group	*Pnma* (62)	No. parameters	61
Color/habit	Colorless blocks	R_1 (obs)	0.0295
Size (mm)	$0.08 \times 0.09 \times 0.13$	wR_2 (all data)	0.0781
a (Å)	6.882(1)	S	1.14
b (Å)	6.964(1)	Min.–max. resd. (e Å^{-3})	−0.27, 0.27
c (Å)	12.306(2)	Device type	Oxford Xcalibur3 CCD
$\lambda_{MoK\alpha}$ (Å)	0.71073	Solution	SIR-97
T (K)	200	Refinement	SHELXL-97
Theta min–max (°)	4.4, 26.0	Absorption correction	Multi-scan
Data set (h; k; l)	−6:8; −8:8; −15:15	CCDC No.	791757
Reflection collected	2,877		

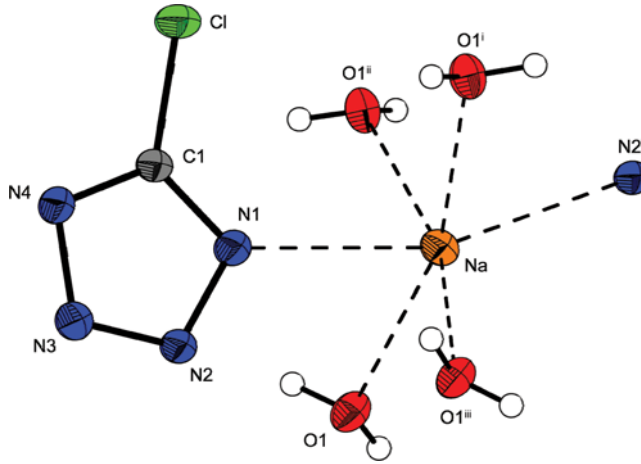


Figure 1. Molecular structure and coordination sphere of the sodium atoms in the structure of **3**. Thermal ellipsoids are drawn at the 50% probability level, and H atoms are shown as spheres of arbitrary radii. Selected distances (Å): Cl–C1 = 1.706(2), Na–O1 = 2.419(1), Na–O1^{iii} = 2.419(1), Na–O1^{i} = 2.428(1), Na–O1^{ii} = 2.428(1), Na–N1 = 2.574(2), N2–N3 = 1.314(3), N2–N1 = 1.350(3), N3–N4 = 1.349(3), N1–C1 = 1.331(3), N4–C1 = 1.319(3); (i) $0.5 + x$, $0.5 - y$, $1.5 - z$; (ii) $0.5 + x$, y, $1.5 - z$; (iii) x, $0.5 - y$, z (color figure available online).

[25] and were modified according to instruction [26] using a Bundesanstalt für Materialforschung (BAM [27]) drop hammer (Deichel & Partner GmbH, Germany) [28]. The friction

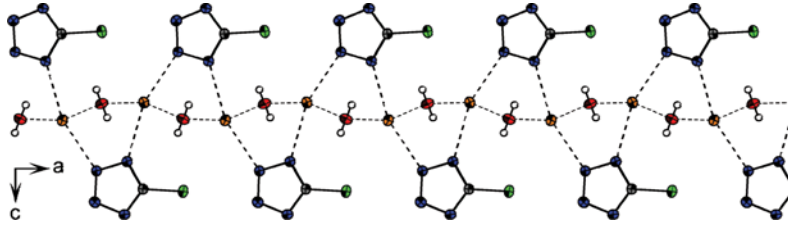


Figure 2. Formation of chains along the *a* axis in the structure of **3**. View along the *b* axis (color figure available online).

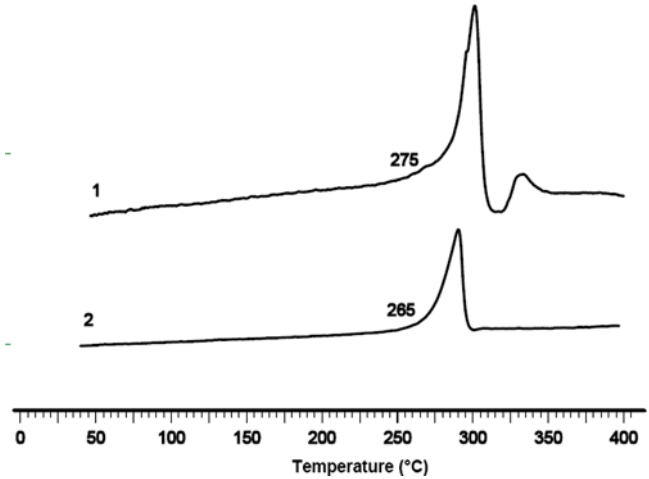


Figure 3. DSC plots of **1** and **2** at a heating rate of $5^{\circ}\mathrm{C\,min^{-1}}$ (Exo up). T_{dec} (°C): **1**, 275; **2**, 265 (color figure available online).

sensitivities were carried out according to STANAG 4487 [29] and were modified according to instruction [30] using a BAM friction tester. Electrostatic sensitivity tests were carried out on a small-scale electric spark tester ESD 2010EN (OZM Research, Czech Republic) operating with the Winspark 1.15 Software Package [31] Both **1** and **2** are classified as ''very sensitive'' according to the *UN Recommendations on the Transport of Dangerous Goods* [32] in terms of both friction and impact sensitivity (impact: insensitive $>40\,\mathrm{J}$, less sensitive $\geq 35\,\mathrm{J}$, sensitive $\geq 4\,\mathrm{J}$, very sensitive $\leq 3\,\mathrm{J}$; friction: insensitive $>360\,\mathrm{N}$, less sensitive $= 360\,\mathrm{N}$, sensitive $<360\,\mathrm{N} > 80\,\mathrm{N}$, very sensitive $\leq 80\,\mathrm{N}$, extremely sensitive $\leq 10\,\mathrm{N}$). Both **1** and **2** are slightly more sensitive than lead azide in terms of impact and comparable within the limits of our instrumentation in friction sensitivities [33]. The advantages of **1** or **2** relative to lead azide become apparent when comparing the sensitivities toward electrostatic discharge (ESD). Lead azide has an ESD sensitivity of only 3 mJ [34], a value easily achieved by the human body, making handling extremely hazardous, whereas **1** and **2** are

only sensitive to 25 and 20 mJ, respectively. These values are at the upper limit of what the human body can generate (∼25 mJ), offering a distinct margin of safety present compared to the use of lead azide. Table 2 presents the sensitivities of **1** and **2** compared to lead azide.

Flame test results of **1** and **2** provided similar results, with smaller amounts crackling with the presence of a blue–green flame and larger amounts detonating. To characterize the ability of the materials to detonate, plate dent tests [24] were performed with each compound. Into a 0.6-cm-ID copper detonator body 0.12 g of each primary explosive was lightly pressed to a density of 0.85 g cm^{-3}. Using a commercial electric igniter type A (Schäffler & Co. KG, Austria) the samples were detonated against a 1-mm-thick aluminum plate. Compound **1** gave a dent in the plate comparable to the vigorous initiator silver acetylide-nitrate double salt [5], whereas **2** was noticeably less energetic, with a decreased dent in the aluminum plate. Figure 4 shows the remnants of the copper tube detonator bodies where the banana peeling of the copper is noticeably more significant for **1** compared to **2**.

The ability of small amounts of **1** and **2** to explode under the influence of laser ignition was determined by confining several milligrams of each primary explosive in a glass melting point tube and illuminating each with a 658-nm, 200-mW red laser. Both compounds exploded instantly upon illumination. A video of the laser initiation of **1** is available online at http://www.cup.uni-muenchen.de/ac/klapoetke/content/supplementary/videos/LaserIgnition5.wmv.

Table 2
Sensitivities of **1** and **2** compared to lead azide

	1	**2**	$Pb(N_3)_2$
Impact (J)	<1	<1	2.5[33]
Friction (N)	<5	<5	0.1[33]
ESD (mJ)	25	20	3[34]

Figure 4. Detonator bodies after detonation of 100 mg of **1** and **2** (color figure available online).

Experimental

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Germany) if not stated otherwise. Chlorotetrazole and bromotetrazole were prepared according to the literature procedures [35]. Decomposition points were measured with a Linseis PT10 DSC using a heating rate of $5°C\,min^{-1}$ and were checked with a Büchi Melting Point B-450 apparatus. Infrared spectra were recorded using a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) instrument. Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. The impact and friction sensitivity data was determined using a BAM drop hammer and a BAM friction tester, and electrostatic sensitivity was determined using a electric spark tester ESD 2010EN (OZM Research, Czech Republic) operating the Winspark 1.15 software package.

> CAUTION: Copper (II) halotetrazolates **1** and **2** are primary explosives of high sensitivity toward various stimuli. Proper personal protective equipment should be used at all times (face shield, goggles, ear protection,

body armor, conductive equipment, Kevlar gloves and arm shields).

Copper (II) Chlorotetrazolate (1)

Copper sulfate (0.40 g, 1.6 mmol) was dissolved in 5 mL distilled water. To this was added a solution of 0.42 g (3.2 mmol) of chlorotetrazole and 1.6 mL 2 M NaOH. The resulting blue precipitate was centrifuged and resuspended in 5 mL distilled water followed by centrifugation. This process was repeated three times to obtain 0.42 g (91%) of **1**. $T_{dec} = 275°C$; IR (cm^{-1}) $v = 3200$ (w, broad), 1442 (w), 1390 (m), 1376 (s), 1358 (s), 1246 (w), 1202 (w), 1182 (w), 1088 (w), 1068 (w), 1038 (w), 721 (w) cm^{-1}; EA ($CuC_2N_8Cl_2$, 246.51). Calcd.: C, 8.88; N, 41.42. Found: C, 9.21; N, 40.24. BAM impact: <1 J, BAM friction: <5 N; ESD: 25 mJ.

Copper (II) Bromotetrazolate (2)

Copper sulfate (0.20 g, 0.80 mmol) was dissolved in 5 mL distilled water. To this was added a solution of 0.62 g (1.6 mmol) of bromotetrazole and 0.8 mL 2 M NaOH. The resulting blue precipitate was centrifuged and resuspended in 5 mL distilled water followed by centrifugation. This process was repeated three times to obtain 0.26 g (90%) of **2**. $T_{dec} = 265°C$; IR (cm^{-1}) $v = 1436$ (w), 1356 (m), 1335 (s), 1240 (w), 1190 (w), 1173 (w), 1062 (w), 1031 (m), 713 (w) cm^{-1}; EA ($CuC_2N_8Br_2$, 359.43). Calcd.: C, 6.68, N, 31.18%. Found: C, 6.62; N, 31.37%. BAM impact: <1 J, BAM friction: <5 N; ESD: 20 mJ.

Sodium 5-Chlorotetrazolate Dihydrate (3)

Chlorotetrazole (0.42 g, 3.2 mmol) was dissolved in 1.6 mL of 2 M NaOH and the solution was allowed to evaporate, yielding 0.48 g (92%) of **3** as colorless crystals. $T_{dec} = 315°C$; IR (cm^{-1}) $v = 3507$ (m), 3407 (m), 3251 (w), 1664 (w), 1624 (m), 1458 (w), 1376 (m), 1353 (s), 1195 (m), 1126 (m), 1093 (w), 1044 (m), 1012 (w), 724 (m); ^{13}C NMR (DMSO d_6) δ (ppm) = 150.8

(s, 1C, CN_4Cl); EA ($Na_2CN_4Cl(H_2O)_2$, 162.51). Calcd.: C, 7.39; N, 34.48; H, 2.48%. Found: C, 7.31; N, 34.36; H, 2.45%.

Conclusions

From this experimental work, the following conclusions can be drawn:

- Copper (II) chloro and bromotetrazolates are easily prepared from the corresponding halotetrazole and a copper salt in high yield.
- The impact and friction sensitivities of the copper halotetrazolates are comparable to (friction) or slightly higher (impact) than those of lead azide; however, the ESD sensitivity of each is lower than lead azide.
- Copper (II) chlorotetrazolate exhibits performance similar to other primaries in the plate dent test. Copper (II) bromotetrazolate exhibits inferior performance.
- Both copper (II) chloro and bromotetrazolates are laser-ignitable primary explosives.
- The chlorotetrazolate anion adopts a similar structure to that of cesium cyanotetrazolate anion.

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Full Paper

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Salts of Tetrazolone – Synthesis and Properties of Insensitive Energetic Materials

Dennis Fischer,[a] Thomas M. Klapötke,*[a] and Jörg Stierstorfer[a]

Abstract: Tetrazolone (5-oxotetrazole, **1**) is formed by diazotization of 5-aminotetrazole in the presence of $CuSO_4$. Nitrogen-rich salts such as guanidinium (**2**), 1-aminoguanidinium (**3**), 1,3-diamino-guanidinium (**4**), 1,3,5-triamino-guanidinium (**5**), ammonium (**6**), hydrazinium (**7**) and the hydroxylammonium (**8**) salts of tetrazolone were prepared by facile deprotonation or metathesis reactions. All compounds were characterized by single-crystal X-ray diffraction, vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis and DSC measurements. The heats of formation of **2–8** were calculated using the atomization method based on CBS-4M enthalpies. With these values and the experimental (X-ray) densities several detonation parameters such as the detonation pressure, velocity, energy and temperature were computed using the EXPLO5 code (V.5.04). In addition, the sensitivities towards impact, friction and electrical discharge were tested using the BAM drop hammer and friction tester as well as a small scale electrical discharge device.

Keywords: Tetrazoles · Secondary explosives · Crystal structures · Detonation parameters · Sensitivities

1 Introduction

Research towards insensitive replacements of hexogen (RDX) and nitropenta (PETN) is still of particular interest in our research group. RDX has been identified as toxic and possibly carcinogenic [1]. PETN is weaker in toxicity, but shows high sensitivities when used as a secondary explosive [2]. Therefore, both compounds must be replaced by "greener" alternatives. An appropriate explosive must achieve high performance while maintaining chemical and thermal stability. Additionally, current research efforts in the energetics community are focused on developing ingredients with minimal responses to impact, friction and electrostatic discharge. The term "Insensitive Munition (IM)" is used to describe munitions, which are particularly safe to handle and which are difficult to initiate accidentally, but at the same time have the power and reliability to fulfill the requirements to complete the mission [3]. The current most prominent candidates in use are FOX-7 [4], NTO (5-nitro-1,2,4-triazole-3-one) [5], and TATB (2,4,6-triamino-1,3,5-trinitro-benzene) [6] (Figure 1).

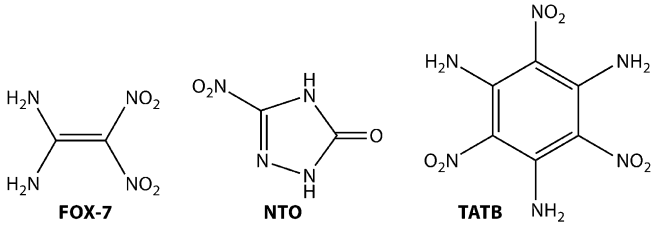


Figure 1. Prominent insensitive secondary explosives.

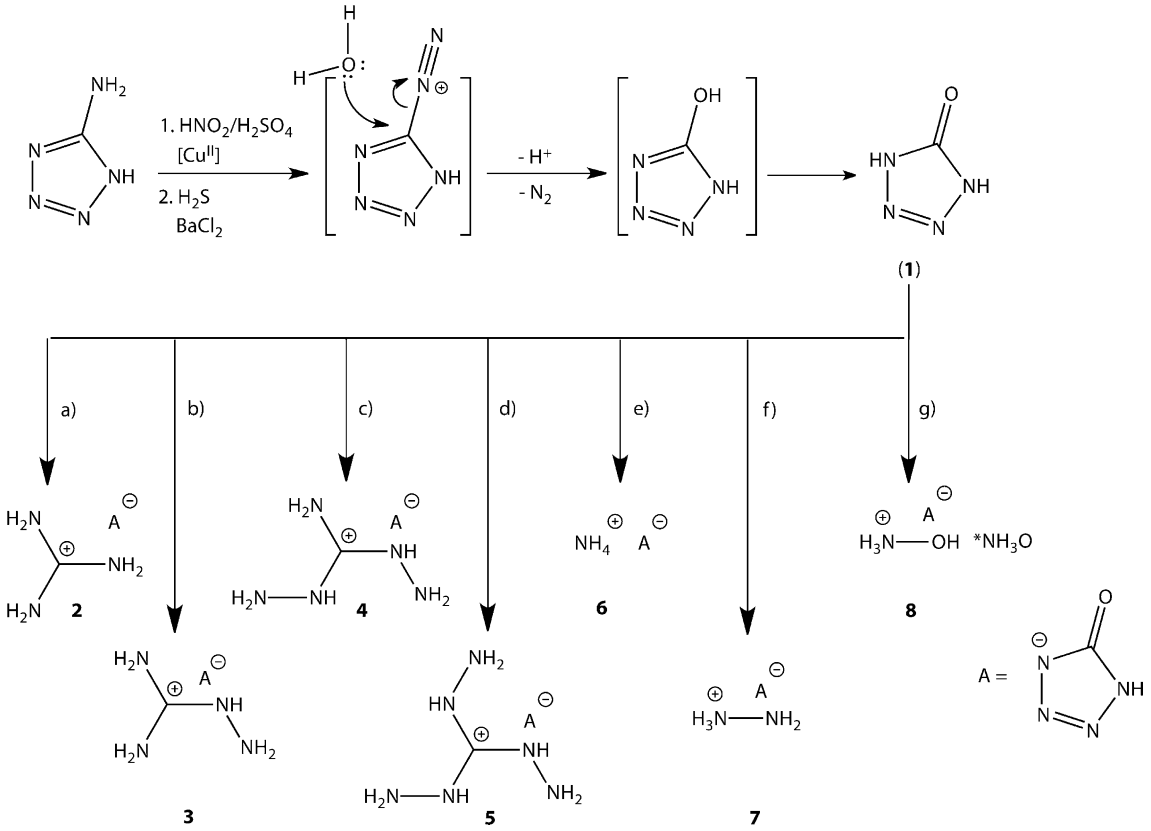
The research on energetic tetrazole derivatives in our group yielded numerous mostly very powerful compounds (based on their high heat of formation) but also oftentimes showing high sensitivities [7]. Here we report on a series of nitrogen-rich salts of 5-oxotetrazole [8], which show acceptable very low sensitivities and thermal stabilities in combination with good calculated detonation parameters.

2 Results and Discussion

2.1 Synthesis

The synthesis of tetrazolone (**1**) as shown in Scheme 1 involves the diazotization of 5-aminotetrazole in acidic medium and the subsequent decomposition of the formed tetrazole diazonium sulfate, which is catalyzed by Cu^{II}. Compound **1** is isolated after removing the copper in the form of CuS and the sulfate as $BaSO_4$. Because of the explosive nature of the tetrazole diazonium cation the diazotization is carried out in dilute sulfuric acid at 0 °C with a ratio of water/diazonium salt of approximately 1000/1. *High concentrations of this solution or pure diazo-tetrazole ends up in violent explosions!* Even under the normal reaction conditions there are sometimes "micro explosions" in the reaction flask noticeable by a crackling noise. It was found that

[a] *D. Fischer, T. M. Klapötke, J. Stierstorfer*
Energetic Materials Research, Department of Chemistry, University of Munich (LMU), Butenandtstr. 5–13, 81377 Munich, Germany
**e-mail: tmk@cup.uni-muenchen.de*



Scheme 1. Synthesis of 5-oxotetrazole by decomposition of the tetrazoldiazonium cation in aqueous solution and synthesis of the monodeprotonated oxo-tetrazolate salts. Reaction conditions: a) Guanidinium carbonate/H_2O/50 °C/10 min; b) aminoguanidinium hydrogen carbonate/H_2O/50 °C/10 min; c) $Ba(OH)_2$, diaminoguanidinium bishydrogensulfate/H_2O/100 °C/10 min, d) triaminoguanidine/EtOH/50 °C/1 min; e) NH_3/H_2O/RT/1 min, f) $N_2H_4{\cdot}H_2O/H_2O$/RT/1 min; g) NH_2OH/H_2O/RT/1 min.

this effect can be minimized by using exactly one equivalent of nitrite instead of 1.1 equivalents as described in the literature procedure [8]. The possible reaction mechanism of the decomposition of a tetrazoldiazonium cation in aqueous solution which leads to tetrazolone is also depicted in Scheme 1. It is a Sandmeyer type reaction which involves water attacking the diazonium cation by the release of dinitrogen. There are also other possible decomposition mechanisms of this diazonium cation, e.g. the release of dinitrogen leaving a highly reactive tetrazolyl cation which decomposes spontaneously. This could be a possible reason for the low yield of 31 %.

Compound **1** has two acidic protons and can therefore be doubly deprotonated. Although showing a very low field shifted ^{1}H NMR spectrum which is usually measured for very acidic tetrazoles like 5-nitriminotetrazole [9] only strong or medium strong bases like guanidine or triaminoguanidine are able to deprotonate **1**. Attempts to deprotonate **1** with weak bases like diaminourea [10] using a 1 : 1 stoichiometry yielded only **1** and colorless solids of various constitutions. Only the single deprotonated salts of **1** (Scheme 1) were synthesized in this work. Compound **1** can also be alkylated at the 1 and 4 position, which has been done in our group [11]. The general synthesis of salts **2–8** was carried out in water or ethanol. For the synthesis of **5–8** the free base and for the synthesis of **2–4** the carbonate and hydrogen carbonate of the corresponding cation were added to a solution of **1**. After short reaction times the solvent was removed. Also an excess of ammonia solution yielded only monodeprotonated **6**. An equimolar aqueous hydroxylamine solution did not result in deprotonation of **1**. However, a stoichiometry of 2 : 1 yielded the monodeprotonated salt **8** under inclusion of one molecule hydroxylamine in isomeric ammonium N-oxide form (Figure 10). Diaminoguanidinium 5-oxotetrazolate was synthesized in two steps. First the monodeprotonated barium salt was generated by the addition of 0.5 equiv. of $Ba(OH)_2$ to an aqueous solution of **1**. In the second step 0.5 equiv. of bis(diaminoguanidinium) sulfate were added under precipitation of $BaSO_4$. The triaminoguanidinium salt **5** was synthesized using the free base triaminoguanidine in ethanol.

2.2 Crystal Structures

Suitable single crystals of the described compounds (**2–8**) were mounted in Kel-F oil and transferred to the N_2 stream of an Oxford Xcalibur3 diffractometer with a Spellman gen-

erator (voltage 50 kV, current 40 mA) and a KappaCCD detector using a $\lambda_{Mo-K\alpha}$ radiation wavelength of 71.073 pm. All structures were measured at −100 °C (see also Table 1). The data collection and data reduction was carried out with the CrysAlisPro software [12]. The structures were solved with SIR-92 [13] or SHELXS-97 [14] refined with SHELXL-97 [15] and finally checked using the PLATON software [16] integrated in the WINGX software suite [17]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions were corrected by a SCALE3 ABSPACK multi-scan method [18]. In the case of the chiral space groups *Fdd*2 (**6**) and $P2_1$ (**8**) the "Friedel pairs" have been merged using the SHELX command "MERG 4".

Crystals of guanidinium 5-oxotetrazolate (**2**) suitable for X-ray analysis were obtained from water. Compound **2** crystallizes in the monoclinic space group $P2_1/n$ with four molecules in the unit cell and a cell volume of 5981700 pm^3.

Table 1. X-ray data and parameters.

	2	**3**	**4**	**5**·2H$_2$O	**5**	**6**	**7**	**8**
Formula	$C_2H_7N_7O$	$C_2H_8N_8O$	$C_2H_9N_9O$	$C_2H_{14}N_{10}O_3$	$C_2H_{10}N_{10}O$	CH_5N_5O	CH_6N_6O	$CH_8N_6O_3$
FW/g mol^{-1}	145.12	160.14	175.15	226.20	190.17	103.08	118.10	152.13
Crystal system	monoclinic	monoclinic	triclinic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Space Group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	*Fdd*2 (No. 43)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
Color/ Habit	colorless rod	colorless block	colorless block	colorless block	colorless rods	colorless rods	colorless rods	colorless block
Size/mm	0.16×0.17×0.20	0.10×0.20×0.30	0.15×0.19×0.21	0.21×0.22×0.26	0.14×0.20×0.23	0.05×0.07×0.10	0.07×0.08×0.21	0.18×0.19×0.20
a/ppm	355.13(3)	499.50(3)	663.12(8)	684.10(6)	748.06(3)	1574.5(6)	359.10(7)	674.58(7)
b/ppm	1750.46(15)	1784.39(13)	669.52(7)	836.69(7)	692.20(3)	2770.0(9)	1503.4(3)	492.43(4)
c/ppm	978.21(11)	753.79(6)	921.41(11)	944.68(7)	1525.25(7)	404.37(17)	912.0(2)	949.75(9)
α/°	90	90	70.794(10)	84.078(7)	90	90	90	90
β/°	100.365(9)	94.010(7)	73.082(10)	73.972(7)	100.161(4)	90	92.03(2)	101.453(10)
γ/°	90	90	68.082(10)	75.711(7)	90	90	90	90
V/pm^3	5981700(1000)	6702100(800)	3517200(800)	5032600(800)	7774000(600)	1763600(1200)	4920500(1700)	3092100(500)
Z	4	4	2	2	4	16	4	2
$\rho_{calcd.}$/ g cm^{-3}	1.612	1.587	1.654	1.493	1.625	1.553	1.594	1.634
μ/mm^{-1}	0.132	0.130	0.135	0.129	0.133	0.132	0.134	0.150
F(000)	304	336	184	240	400	864	248	160
θmin-max/ °	4.2, 26.0	4.2, 26.5	4.5, 27.0	4.3, 26.5	4.4, 26.5	5.1, 26.0	4.5, 26.0	4.4, 27.0
Dataset *h*; *k*; *l*	−4 : 4; −21 : 21; −10 : 12	−6 : 5; −11 : 22; −9 : 7	−8: 7; −8: 8; −10 : 11	−8 : 8; −10 : 10; −11 : 11	−9 : 9; −8 : 6; −19 : 18	−17 : 19; −24 : 34; −4 : 4	−4 : 3; −18 : 18; −6 : 11	−8 : 8; −6 : 6; −7 : 12
Reflect. coll.	3824	2440	2462	5351	5483	2154	1813	1748
Independ. refl.	1178	1377	1509	2078	1606	488	969	753
R_{int}	0.042	0.024	0.025	0.029	0.036	0.066	0.036	0.034
Reflection obs.	736	981	985	1454	1110	295	487	555
No. parameters	119	132	145	192	158	84	97	76
R_1 (obs)	0.0340	0.0326	0.0360	0.0340	0.0333	0.0406	0.0430	0.0318
wR_2 (all data)	0.0638	0.0703	0.0697	0.0802	0.0743	0.0907	0.0737	0.0615
S	0.82	0.90	0.86	0.90	0.89	0.83	0.75	0.85
Resd. dens./ e ppm^{-3}	−0.16×10^{-6}, 0.18×10^{-6}	−0.19×10^{-6}, 0.15×10^{-6}	−0.20×10^{-6}, 0.19×10^{-6}	−0.22×10^{-6}, 0.17×10^{-6}	−0.20×10^{-6}, 0.23×10^{-6}	−0.19×10^{-6}, 0.24×10^{-6}	−0.22×10^{-6}, 0.18×10^{-6}	−0.19×10^{-6}, 0.19×10^{-6}
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92	SIR-92	SIR-92	SIR-92	SIR-92	SHELXS-97	SIR-92	SHELXS-97
Refinement	SHELXL-97	SHELXS-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
CCDC	815777	815772	815773	815774	815775	815776	815770	827687

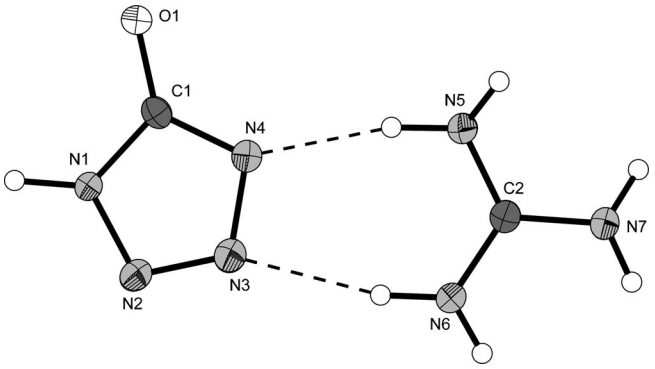


Figure 2. Molecular moiety of **2**. Ellipsoids are drawn at the 50% probability level. Selected bond distances and angles in the anion of 2: bond lengths/pm: O1–C1 127.5(2), N1–C1 135.9(2), N4–C1 134.8(2), N1–N2 135.7(2), N2–N3 129.8(2), N3–N4 136.2(2); angles/°: O1–C1–N1 125.17(15), O1–C1–N4 127.98(16), N1–N4 106.86(15), N2–N1–C1 109.35(14), N1–N2–N3 106.10(13); torsion angles/°:C1–N1–N2–N3 −0.62(18), N2–N1–C1–O1 −179.39(14).

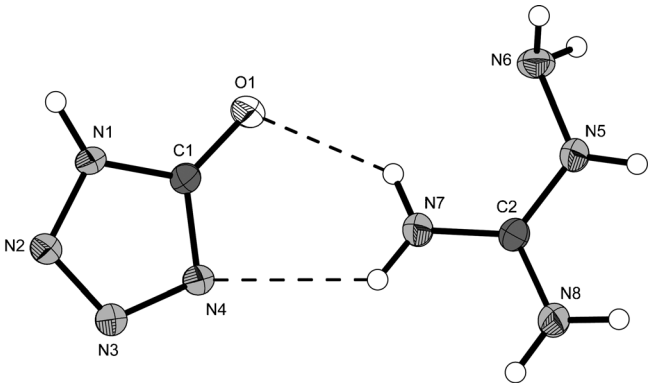


Figure 3. Molecular moiety of **3**. Ellipsoids are drawn at the 50% probability level.

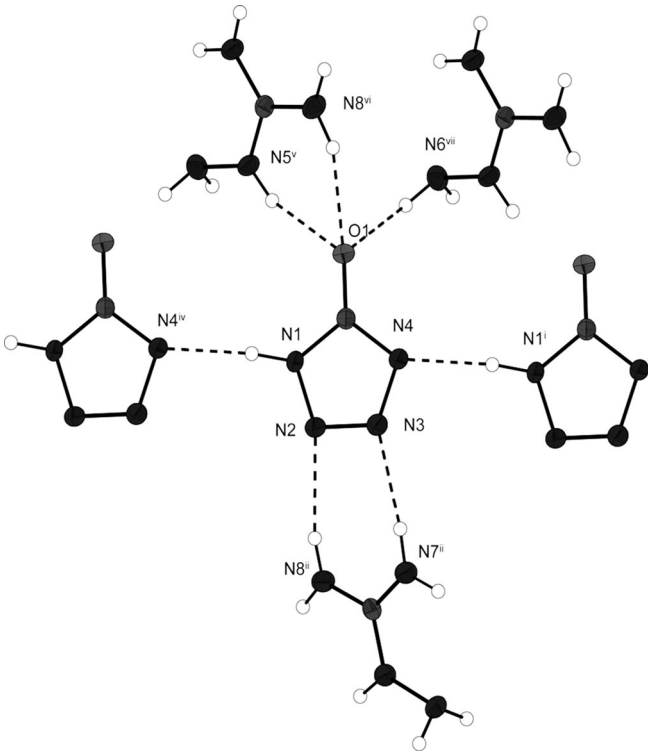


Figure 4. View of the hydrogen bonds of one tetrazolone anion in **3**. (i) $1+x, y, z$; (ii) $-x, -y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $-1+x, y, z$; (v) $-1+x, 0.5-y, -0.5+z$; (vi) $-1+x, 0.5-y, -0.5+z$; (vii) $x, 0.5-y, -0.5+z$.

Compound **2** has a density of 1.612 g cm^{-3}. The molecular unit is shown in Figure 2. The 5-oxotetrazolate anions form dimers connected by hydrogen bonds similar to the crystal structure of **4** depicted in Figure 6. The structures of the cations follow the structures of comparable nitrogen-rich salts of tetrazoles in the literature [19]. The bond lengths and angles are similar in all of the investigated compounds and are partially listed in the caption of Figure 2. The C–O bond length is 127.5(2) pm, which is 7 pm longer than the standard C=O double bond [20], indicating the tetrazolone – 5-hydroxytetrazole tautomerism. The C–N1 and the C–N4 bond lengths are 136 pm and 135 pm, respectively, which is between a standard C–N single bond length (147 pm) and a standard C=N double bond length (122 pm) indicating an aromatic system. The N1–N2 and N3–N4 bond lengths (approx. 136 pm) follow this trend. The N2–N3 bond (130 pm) is slightly shorter than the other N–N bonds in the ring and is in good agreement with the Lewis structure of the 5-oxotetrazolate anion and also with other tetrazolates in the literature [21].

Crystals of aminoguanidinium 5-oxotetrazolate (**3**) suitable for X-ray analysis were obtained from water. Compound **3** crystallizes in the monoclinic space group $P2_1/c$ with four anion/cation pairs in the unit cell. The density is 1.587 g cm^{-3}, which is slightly lower than that of **2**. Compound **3** contains a network of hydrogen bonds with D···A distances ranging from 282.5 pm to 318.4 pm as shown in Figure 3 and Figure 4.

Crystals of the diaminoguanidinium 5-oxotetrazolate (**4**), depicted in Figure 5 and suitable for X-ray analysis were grown in water. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecular units in the unit cell.

The density of **4** is 1.654 g cm^{-3} and the cell volume is 3517200 pm^3. The 5-oxotetrazolate units in this structure form dimers connected by hydrogen bonds like in **2**. The center of inversion is surrounded by the 5-oxotetrazolate dimer as shown in Figure 6.

Two different structures of triaminoguanidinium 5-oxotetrazolate were determined. Crystallization from water yielded the dihydrate (**5**·2H_2O) which crystallizes in the triclinic space group $P\bar{1}$ with two molecular units in the unit cell and a calculated density of 1.493 g cm^{-3}. The molecular unit is shown in Figure 7. The formation of 5-oxotetrazolate

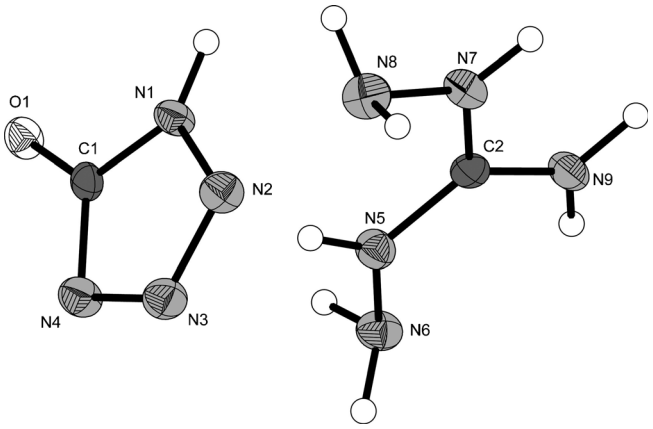


Figure 5. Molecular moiety of **4**. Ellipsoids are drawn at the 50% probability level.

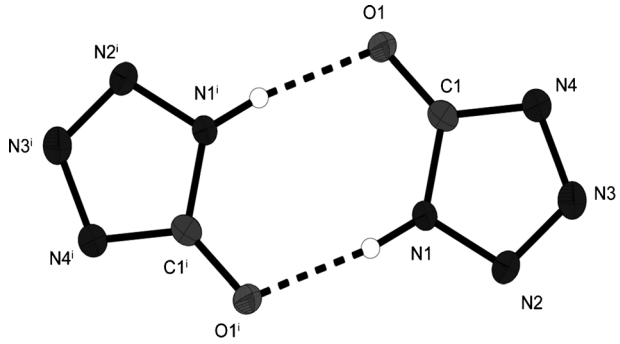


Figure 6. 5-Oxotetrazolate dimers in **4**. (i) $-x, 2-y, 1-z$.

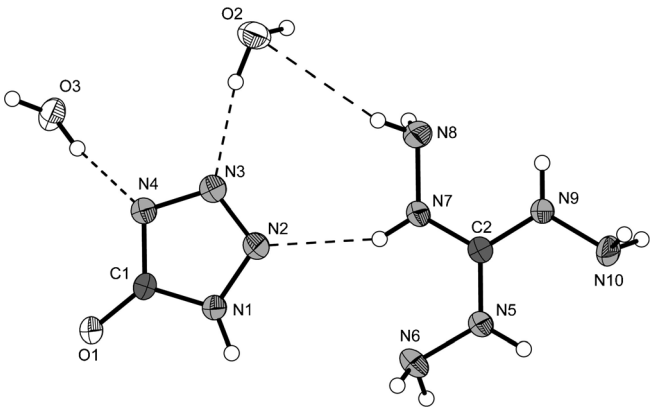


Figure 7. Molecular moiety of **5**·2H_2O. Ellipsoids are drawn at the 50% probability level.

dimers as in the structure of **2** and **4** can also be observed in this structure.

Crystals of water free triaminoguanidinium 5-oxotetrazolate (**5**) suitable for X-ray analysis were grown in ethanol. Compound **5** crystallizes in the monoclinic pace group $P2_1/c$ with four molecular units in the unit cell, a cell volume of 7774000 pm^3 and a density of 1.625 g cm^{-3}. The molecular moiety is shown in Figure 8. Again the motif of 5-oxotetrazolate dimers as in **2**, **4** and **5**·2H_2O is observed here.

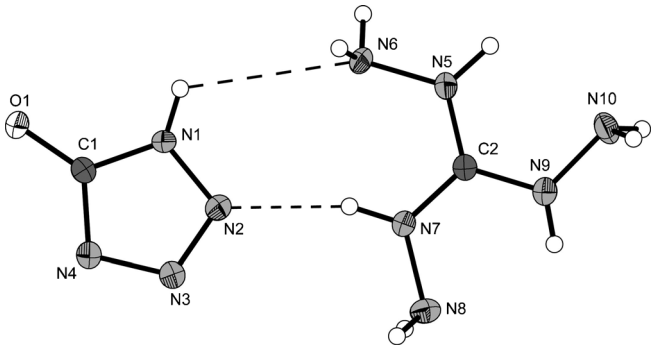


Figure 8. Molecular moiety of **5**. Ellipsoids are drawn at the 50% probability level.

Crystals of ammonium 5-oxotetrazolate (**6**) suitable for X-ray analysis were obtained by dissolving **1** in hot ethanol and diffusing NH_3 from 25% aqueous NH_3 into the solution. Compound **6** crystallizes in the orthorhombic space group *Fdd*2 with 16 molecular units in the unit cell and a cell volume of 17635000 pm^3. The molecular unit is shown in Figure 9. Again the structure is dominated by several strong hydrogen bonds.

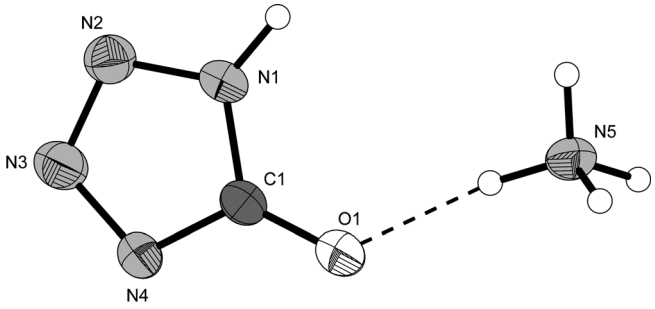


Figure 9. Molecular moiety of **6**. Ellipsoids are drawn at the 50% probability level.

Single crystals of hydrazinium 5-oxotetrazolate (**7**) were obtained from water. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ with four molecular units in the unit cell. Its calculated density is 1.594 g cm^{-3}. The molecular unit is shown in Figure 10.

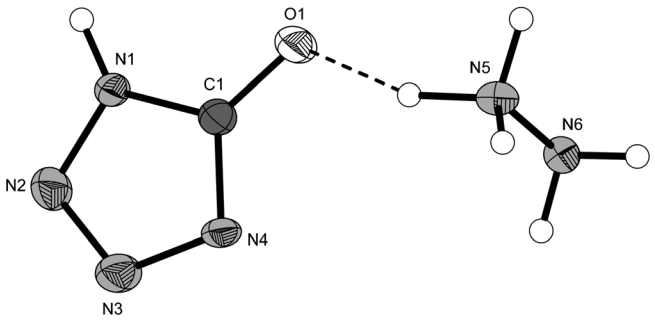


Figure 10. Molecular moiety of **7**. Ellipsoids are drawn at the 50% probability level.

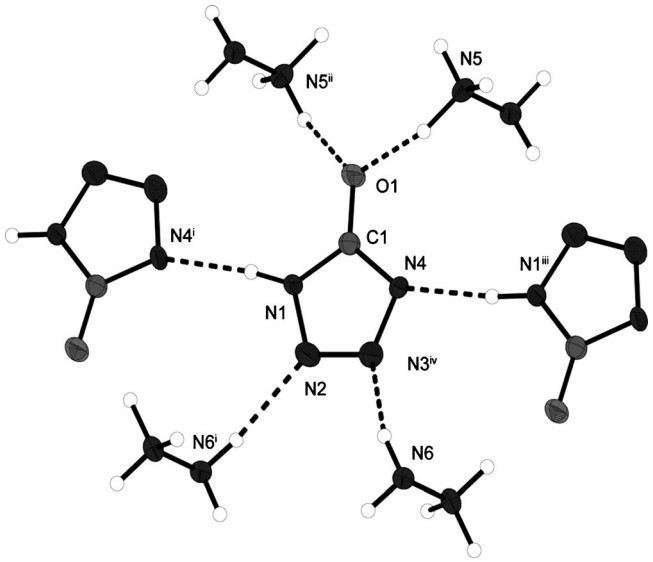


Figure 11. Coordination of the 5-oxotetrazolate anion in **7** by hydrogen bonds. (i) $-0.5+x$, $0.5-y$, $0.5+z$; (ii) $2-x$, $1-y$, $1-z$; (iii) $0.5+x$, $0.5-y$, $-0.5+z$; (iv) $2.5-x$, $-0.5+y$, $0.5-z$.

The network of hydrogen bonds is shown in Figure 11. Except for the carbon atoms all atoms participate in hydrogen bonds. In accordance to the structure of **6**, the hydrazinium salt **7** forms chains of 5-oxotetrazolate units which are coordinated by hydrogen bonds to the hydrazinium cations and ammonium cations, respectively.

In the structure of hydroxylammonium 5-oxotetrazolate (**8**), one zwitterionic hydroxylamine (better described as ammonium N-oxide) is included (Figure 12). Interestingly,

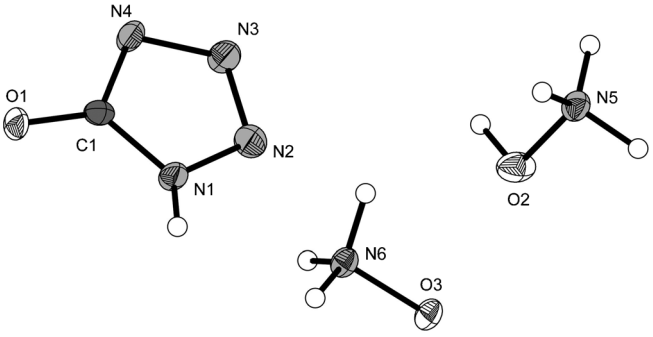


Figure 12. Molecular moiety of **8**·NH_3O. Ellipsoids are drawn at the 50% probability level.

the N–O bond lengths O2–N5 = 141.97(10) pm and N6–O3 = 141.98(10) pm are nevertheless equal. The density of 1.634 g cm^{-3} is one of the highest observed in this work and is only be surpassed by **4** (1.654 g cm^{-3}).

2.3 NMR Spectroscopy

The ^{1}H NMR spectrum of **1** exhibits a singlet signal according to the C_{2v}-symmetry which can be observed in lower fields at $\delta = 14.05$ ppm. The ^{15}N NMR spectrum reveals only two signals at -31.2 for N1 and N4 and -181.3 ppm for N2 and N3 which is a quite common shift for tetrazoles [11]. A coupling between the protons and N1 and N4 could not be observed which confirms the acidic nature of the protons. The ^{13}C NMR shift of **1** is 154.2 ppm and also quite common for a tetrazole [11]. The ^{13}C NMR shifts of **2**, **3** and **5** range from 167.1 ppm for the aminoguanidinium salt to 167.3 ppm for the guanidinium salt. In total the ^{13}C shift of the anion ranges from 159.8 ppm for the triaminoguanidinium salt to 160.3 ppm for the aminoguanidinium salt. The ^{1}H NMR spectrum of **5** shows two broad singlet signals at $\delta = 9.05$ ppm and 4.63 ppm according to the NH and NH_2 protons. One would expect one further signal for the other proton of the 5-oxotetrazolate anion which cannot be observed underlining the acidic nature of this proton undergoing fast exchange processes. An evidence for these processes is given in the ^{1}H NMR spectrum of **3** containing two signals at $\delta = 7.74$ ppm and 4.66 ppm for the NH and NH_2 protons of the cation, respectively, and a very broad signal ranging from 4.2 to 10.2 ppm. The proton NMR spectrum of **2** also shows up two singlet signals at $\delta =$ 7.74 ppm for the cation and 3.85 ppm for water, respectively. Normally, the chemical shift of water in DMSO-d_6 is around 3.3 and is shifted 0.55 ppm more towards lower fields. This is also an evidence for the exchange processes of the acidic protons involved in the system. The ^{13}C NMR shifts of the carbons of **6** and **7** show up at $\delta = 165.4$ ppm and 154.8 ppm. The corresponding ^{1}H NMR spectra consist of singlet signals at $\delta = 6.41$ ppm and 11.79 ppm, respectively. These low field shifted signals again confirm the acidic nature of the protons.

2.4 Energetic Properties

2.4.1 Thermal Behavior (DSC)

Thermoplots of differential scanning calorimetry (DSC) measurements of **1–8** are depicted in Figure 13. In order to determine the melt- and decomposition temperatures approx. 1.5 mg of each energetic material were measured in pierced lid Al-containers with a nitrogen flow of 20 mL min^{-1} with a Linseis PT10 DSC [22]. Calibration was done with standard pure indium and zinc at a heating rate of 5 K min^{-1}. Tetrazolone (**1**) has a higher decomposition temperature (239 °C) than its nitrogen rich salts. This is in contrast to many tetrazole derivatives, in which the tetrazolate anion shows higher decomposition temperature than its neutral mother compound [10]. All of the salts have melting points between 132 °C for the guanidinium salt and 199 °C for the ammonium salt which becomes apparent in the convex behavior of the graphs. Their decomposition temperatures range from 174 °C for the TAG salt, which is the least thermally stable one up to 205 °C for the ammonium salt, which is the most thermally stable.

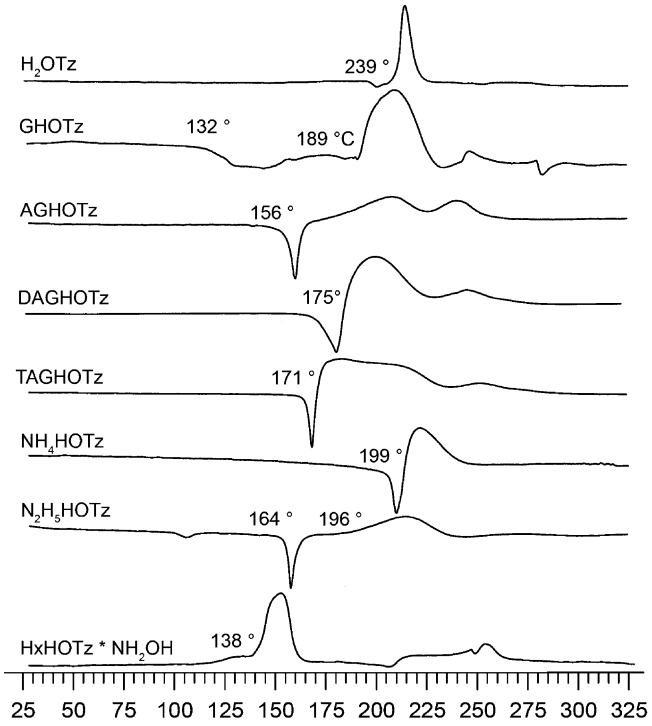


Figure 13. DSC Thermographs of compounds **1–8**.

2.4.2 Sensitivities and Detonation Parameters

Tetrazolone (**1**) and its nitrogen-rich salts are quite insensitive explosives. As shown in Table 2 their impact sensitivities range from 15 J for **5** to more than 40 J for the others. Friction sensitivity is also quite low whereas also **5** is the most sensitive (240 N). According to the UN recommendations on the transport of dangerous goods, compounds bearing a greater impact sensitivity than 40 J and friction sensitivity of 360 N are classified as *insensitive*.

The detonation parameters were calculated using the program EXPLO5 V5.04 [23]. The calculations were performed using the maximum densities according to the crystal structures. Heats of formation were computed theoretically. All calculations were carried out using the Gaussian G09 program package [24]. The enthalpies (*H*) and free energies (*G*) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (M referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections [25]. The enthalpies of the gas-phase species M (Table 3) were computed according to the atomization energy method (Equation (1))[26] described circumstantially in the literature [27].

$$\Delta_f H^\circ_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H^\circ_{(Atoms,\,298)} + \sum \Delta_f H^\circ_{(Atoms,\,298)} \quad (1)$$

Table 2. Energetic parameters of tetrazolone and its nitrogen rich salts.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	CH_2N_4O	$C_2H_7N_7O$	$C_2H_8N_8O$	$C_2H_9N_9O$	$C_2H_{10}N_{10}O$	CH_5N_5O	CH_6N_6O	$CH_8N_6O_3$
FW/g mol^{-1}	86.05	145.12	160.14	175.15	190.17	103.08	118.10	152.13
IS/J [a]	>40	>40	>40	>40	15	>40	>40	>40
FS N [b]	360	>360	>360	>360	240	>360	>252	>360
ESD-test/J [c]	0.6	1	1	0.65	1	1.5	1.5	0.4
N/% [d]	65.11	67.56	69.97	71.97	73.65	67.94	71.16	55.25
Ω/% [e]	−37.18	−71.65	−69.93	−68.50	−67.30	−54.32	−54.19	−31.55
$T_{dec.}$/°C [f]	239	189	179	190	174	205	196	138
Density/g cm^{-3} [g]	1.699	1.612	1.587	1.654	1.625	1.618	1.594	1.634
$\Delta_f H_m^\circ$/kJ mol^{-1} [h]	5	0	116	224	340	16	173	167
$\Delta_f U^\circ$/kJ kg^{-1} [i]	155	125	857	1415	1922	292	1598	1239
Detonation parameters calculated by EXPLO5.04:								
$-\Delta_E U^\circ$/kJ kg^{-1} [j]	2930	2277	2889	3344	3767	3039	4107	6151
T_E/K [k]	2586	1909	2200	2376	2575	2315	2777	3716
p_{CJ}/Pa [l]	207×10^8	182×10^8	202×10^8	244×10^8	254×10^8	217×10^8	253×10^8	324×10^8
D/m s^{-1} [m]	7401	7257	7586	8161	8308	7749	8284	9034
Gas vol./L kg^{-1} [n]	779	825	841	855	867	871	887	933

a) Impact sensitivity (BAM drophammer [30], 1 of 6); b) friction sensitivity (BAM friction tester [30], 1 of 6); c) electrostatic discharge device (OZM [31]); d) nitrogen content; e) oxygen balance; f) decomposition temperature from DSC ($\beta = 5$ K min^{-1}); g) estimated from X-ray diffraction; h) calculated (CBS-4 M) heat of formation; i) calculated energy of formation; j) Energy of Explosion; k) explosion temperature; l) detonation pressure; m) detonation velocity; n) assuming only gaseous products.

Table 3. CBS-4 M calculation results and molecular volumes taken from X-ray solution.

M	$-H^{298}$/a.u.	$\Delta_f H^\circ$(g,M)/kJ mol^{-1}	V_M/nm^3
H_2OTz	333.079784	114.6	
H_2OTz^-	332.548057	−22.6	
G^+	205.453192	571.5	
AG^+	260.701802	671.1	
DAG^+	315.949896	771.9	
TAG^+	371.197775	873.6	
NH_4^+	56.796608	635.5	
$N_2H_5^+$	112.030523	773.6	
NH_4O^+	131.863229	686.6	
NH_3O	131.502326	100.8	
2		548.9	0.149
3		648.5	0.168
4		749.8	0.176
5		851.0	0.194
6		613.0	0.110
7		751.0	0.123
8		765.3	0.155

The gas-phase enthalpies of formation ($\Delta_f H^\circ_{(g, M, 298)}$) were converted into the solid state (standard conditions) enthalpies of formation $\Delta_f H_m^\circ$ (Table 2) using either calculated heat of sublimation for **1** (by the Trouton's Rule [28]) or lattice enthalpies for the ionic compounds (**2–8**). Lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes according to Jenkins's equations [29].

Lastly, the molar standard enthalpies of formation (ΔH_m) were used to calculate the molar solid state energies of formation (ΔU_m) according to Equation (2) (Table 2).

$$\Delta U_m = \Delta H_m - \Delta n\, RT \qquad (2)$$

(Δn being the change of moles of gaseous components)

Compound **8** is the most powerful salt in this series having a calculated detonation velocity (D) of 9034 m s^{-1} and a detonation pressure (p_{CJ}) of 324×10^8 Pa. These values are in the range of those of hexogen (D = 8748 m s^{-1}; $p_{CJ} = 348\times10^8$ Pa), which is mostly used in military explosive applications. Including only compounds without inclusion of solvent, compounds **5** (D = 8308 ms^{-1}; $p_{CJ} = 254\times10^8$ Pa) and **7** (D = 8284 m s^{-1}; $p_{CJ} = 253\times10^8$ Pa) show also promising values with respect to their calculated performance on the one hand and their low sensitivities on the other hand side. These values can be compared to commonly used and sensitive PETN (nitropenta) (D = 8320 m s^{-1}; $p_{CJ} = 320\times10^8$ Pa; IS = 5 J) and recently investigated FOX-7 (D = 8213 m s^{-1}; $p_{CJ} = 288\times10^8$ Pa).

3 Conclusions

Tetrazolone (5-oxotetrazole) was prepared by diazotization of 5-aminotetrazole. Its nitrogen rich salts (guanidinium (**2**), aminoguanidinium (**3**), diaminoguanidinium (**4**), triaminoguanidinium (**5**), ammonium (**6**), hydrazinium (**7**), hydroxylammonium (**8**)) were prepared by facile deprotonation or metathesis reactions. All compounds were characterized by low temperature single-crystal X-ray diffraction. They crystallize in common space groups with densities ranging from 1.554 (**6**) to 1.625 g cm^{-3} (**5**). In addition, all salts were characterized by vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis and differential scanning calorimetry. The heats of formation were calculated on the CBS-4M level of theory to be mostly endothermic. With these values and the X-ray densities several detonation parameters were calculated. The salts of tetrazolone have calculated detonation velocities between 7257 m s^{-1} (**2**) and 9034 m s^{-1} (**8**). The sensitivities (impact, friction and electrical discharge) were tested by standard BAM methods. Tetrazolone and its salts are quite insensitive explosives with decomposition points between 174 °C (**5**) and 239 °C (**1**). Interestingly but unfortunately the decomposition temperatures decrease by deprotonation.The impact sensitivities range from 15 J (**5**) to > 40 J. A maximum friction sensitivity of 240 N was measured for compound **5**.

4 Experimental Part

All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting and decomposition points were measured with a Linseis PT10 DSC using heating rates of 5 K min^{-1}, which were checked with a Büchi Melting Point B-450 apparatus. ^{1}H, ^{13}C and ^{15}N NMR spectra were measured with a JEOL instrument. All chemical shifts are quoted in ppm relative to TMS (^{1}H, ^{13}C) or nitromethane (^{15}N). Infrared spectra were measured with a Perkin–Elmer Spectrum One FT-IR instrument. Raman spectra were measured with a Perkin–Elmer Spectrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses (see below) were performed with a Netsch STA 429 simultaneous thermal analyzer. Sensitivity data were determined using a BAM drophammer and a BAM friction tester [30]. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research) operating with the "Winspark 1.15" software package [31].

Tetrazolone (1)

5-Aminotetrazole (2.06 g, 24.2 mmol) was dissolved in a mixture of water (200 mL) and 98 % H_2SO_4 (2.42 mL). The solution was cooled to 0 °C and 20 g of ice were added. Afterwards, a solution of $NaNO_2$ (1.725 g, 26.7 mmol) in water

(10 mL) was added dropwise. After further stirring at 0 °C for half an hour a precooled solution of $CuSO_4 \cdot 5H_2O$ (8.96 g) in water (40 mL) was added. The solution was stirred at 0 °C for 30 min and afterwards kept for 2 days at 7 °C. The suspension was treated with H_2S and CuS was filtered off. The filtrate was heated to 100 °C while stirring and $BaCl_2 \cdot 2H_2O$ (19 g, 77.8 mmol) was added. $BaSO_4$ was filtered off and the filtrate was evaporated to dryness. The residue was extracted with acetone and the solvent removed. The residue was recrystallized from water yielding 650 mg of colorless crystals (31 %). **DSC** (5 K min^{-1}): 239 °C (dec.). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 14.05$ (s, 2 H); **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 154.2$. **^{15}N NMR** (DMSO-d_6, 25 °C, ppm): $\delta = -181.3$ (NH), -31.2. **IR** (atr, cm^{-1}): $\tilde{\nu} = 2978$ (m), 2842 (m), 2729 (w), 1674 (vs), 1453 (w), 1424 (w), 1319 (w), 1054 (m), 983 (s), 827 (s), 772 (s), 741 (vs); **Raman** (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 2824$ (6), 1425 (13), 1353 (7), 1314 (50), 1067 (100), 1055 (61), 778 (44), 767 (56), 507 (16); **EA** (CH_2N_4O, 86.05): calcd.: C 13.96, H 2.34, N 65.11 %; found: C 13.95, H 2.46, N 64.66 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: > 0.6 J.

Guanidinium-5-oxotetrazolate (2)

Tetrazolone (860 mg, 10 mmol) and guanidinium carbonate (900 mg, 5 mmol) were dissolved in water (20 mL) at 70 °C and the solution was left for crystallization. The crystals were collected yielding 1.45 g (100 %) of colorless product. **DSC** (5 K min^{-1}): 132 °C (mp.), 189 °C (dec). **^{1}H NMR** (DMSO-d_6 25 °C, ppm): $\delta = 3.85$ (s, broad), 7.75 (s, broad); **^{13}C{^{1}H} NMR** (DMSO-d_6 25 °C, ppm): $\delta = 159.0$ (C=O), 167.3 (C=N). **IR** (atr, cm^{-1}): $\tilde{\nu} = 3322$ (m), 3069 (s), 2806 (w), 1651 (vs), 1567 (m), 1485 (m), 1381 (s), 1323 (w), 1160 (w), 1050 (w), 992 (w), 879 (w), 789 (w), 769 (w); **Raman** (1064 nm, 300 mW, 25 °C (cm^{-1})): $\tilde{\nu} = 3206$ (8), 2110 (3), 1566 (6), 1433 (6), 1326 (5), 1272 (27), 1165 (3), 1108 (21), 1046 (41), 1005 (100), 770 (28), 550 (21), 534 (22), 513 (13); **EA** ($C_2H_7N_7O$, 145.12): calcd.: C 16.55, H 4.86, N 67.56 %; found: C 15.82, H 4.25, N 67.70 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1 J.

Aminoguanidinium-5-oxotetrazolate (3)

Tetrazolone (860 mg, 10 mmol) and aminoguanidinium hydrogen carbonate (1.36 g, 10 mmol) were dissolved in water (20 mL) at 70 °C and the solution was left for crystallization. The crystals were collected yielding 1.6 g (100 %) of colorless product. **DSC** (5 K min^{-1}): 156 °C (mp.), 179 °C (dec). **^{1}H NMR** (DMSO-d_6 25 °C, ppm): $\delta = 4.67$ (s, broad), 7.75 (s, broad); **^{13}C{^{1}H} NMR** (DMSO-d_6 25 °C, ppm): $\delta = 160.3$ (C=O), 167.1 (C=N). **IR** (atr, cm^{-1}): $\tilde{\nu} = 3316$ (w), 3086 (w), 1613 (vs), 1425 (m), 1325 (w), 1308 (m), 1266 (m), 1202 (w), 1151 (w), 1096 (w), 1047 (s), 1003 (w), 969 (w), 853 (w), 779 (w), 767 (m), 743 (w), 689 (w); **Raman** (1064 nm, 300 mW, 25 °C (cm^{-1})): $\tilde{\nu} = 3319$ (16), 3202 (13), 1620 (10), 1542 (17), 1446 (8), 1311 (7), 1263 (61), 1218 (5), 1152 (4), 1098 (56), 1048 (100), 969 (69), 781 (67), 617 (13), 514 (35), 494 (17); **EA** ($C_2H_8N_8O$, 160.14): calcd.: C 15.00, H 5.04, N 69.97 %; found: C 16.93, H 4.74, N 65.30 %; **BAM** drophammer: > 40 J; **friction tester**: > 360 N; **ESD**: 1 J.

Diaminoguanidinium-5-oxotetrazolate (4)

Tetrazolone (860 mg, 10 mmol), diaminoguanidinium bishydrogensulfate (2.853 g, 10 mmol) and bariumhydroxide octahydrate (6.310 g, 20 mmol) were dissolved in water (50 mL) at 100 °C. The suspension was filtered and the solution was left for crystallization. The crystals were collected yielding 1.40 g (80 %) of colorless product. **DSC** (5 K min^{-1}): 175 °C (mp.), 190 °C (dec.). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 7.86$, 4.60; **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, ppm): $\delta = 166.7$, 160.7. **IR** (atr, cm^{-1}): $\tilde{\nu} = 3366$ (w), 3338 (w), 3305 (m), 3184 (s), 1654 (s), 1615 (vs), 1450 (w), 1354 (w), 1316 (m), 1270 (w), 1168 (w), 1088 (w), 1043 (m), 985 (w), 935 (m), 818 (w), 763 (m); **Raman** (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu} = 3370$ (9), 3335 (21), 3312 (23), 2318 (6), 1676 (14), 1438 (11), 1321 (17), 1275 (60), 1170 (17), 1144 (7), 1092 (54), 1045 (100), 920 (46), 772 (18), 657 (11), 546 (30), 505 (30); **EA** ($C_2H_9N_9O$, 175.15): calcd.: C 13.71, H 5.18, N 71.97 %; found: C 14.13, H 4.91, N 71.36 %; **BAM** drophammer: > 40 J; **friction tester:** > 360 N; ESD: 0.65 J.

Triaminoguanidinium-5-oxotetrazolate (5)

Tetrazolone (860 mg, 10 mmol) and triaminoguanidine (1.04 g) were suspended in hot ethanol (30 mL). A small amount of water was added until the starting material completely dissolved and the solution was left for crystallization. 1.50 g (79 %) of colorless crystals were collected, washed with ethanol and dried. **DSC** (5 K min^{-1}): 171 °C (mp.), 174 °C (dec). **^{1}H NMR** (DMSO-d_6 25 °C, ppm): $\delta = 4.62$ (s, 6 H, broad), 9.05 (s, 4 H); **^{13}C{^{1}H} NMR** (DMSO-d_6 25 °C, ppm): $\delta = 159.7$ (C=O), 167.2 (C=N). **IR** (atr, cm^{-1}): $\tilde{\nu} = 3310$ (m), 3173 (w), 3121 (w), 2899 (w), 1676 (s), 1628 (vs), 1612 (vs), 1571 (m), 1462 (w), 1434 (w), 1372 (w), 1313 (m), 1265 (s), 1157 (s), 1140 (s), 1085 (s), 1036 (s), 1007 (vs), 978 (s), 912 (m), 773 (s); **Raman** (1064 nm, 300 mW, 25 °C (cm^{-1})): $\tilde{\nu} = 3293$ (42), 3208 (28), 1668 (20), 1615 (19), 1402 (25), 1268 (57), 1209 (11), 1145 (27), 1089 (43), 1039 (100), 883 (79), 764 (93), 646 (29), 511 (69), 410 (56); **EA** ($C_2H_{10}N_{10}O$, 190.17): calcd.: C 12.63, H 5.30, N 73.65 %; found: C 13.16, H 5.38, N 73.40 %; **BAM** drophammer: 12 J; **friction tester**: 240 N; **ESD**: 1 J.

Ammonium-5-oxotetrazolate (6)

Tetrazolone (860 mg, 10 mmol) was dissolved in water (20 mL) and 25 % NH_3 (0.8 mL) was added. The solvent was removed and the residue was dried in vacuo yielding 1.03 g (100 %) of colorless product. **DSC** (5 K min^{-1}): 199 °C (m.p.), 205 °C (dec.). **IR** (atr, cm^{-1}): $\tilde{\nu} = 2767$ (m), 1626 (s), 1489 (m), 1442 (s), 1314 (m), 1269 (w), 1174 (w), 1160 (w),

1090 (w), 1052 (vs), 993 (w), 852 (m), 781 (m), 759 (vs), 687 (m); **Raman** (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3041 (12), 2858 (11), 2804 (15), 2702 (12), 1717 (4), 1628 (5), 1450 (7), 1405 (7), 1382 (4), 1315 (10), 1280 (91), 1163 (8), 1105 (55), 1092 (63), 1054 (100), 1001 (19), 786 (41), 547 (13), 470 (4). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): δ = 6.41 (s); **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, ppm): δ = 165.4; **EA** (CH_5N_5O, 103.8): calcd.: C 11.65, H 4.89, N 67.94 %; found: C 12.10, H 4.53, N 67.17 %; **BAM drophammer**: > 40 J; **friction tester**: > 360 N; **ESD**: 1.5 J.

Hydrazinium-5-oxotetrazolate (7)

Tetrazolone (860 mg, 10 mmol) was dissolved in water (30 mL) and hydrazine hydrate (0.484 mL) was added. The solvent was removed under reduced pressure and the remaining solid dried in vacuo yielding 1180 mg (100 %) of a colorless solid. **DSC** (5 K min^{-1}): 164 °C (m.p.), 195 °C (dec.). **IR** (atr, cm^{-1}): $\tilde{\nu}$ = 3280 (w), 3162 (w), 2923 (w), 2630 (s, br), 1611 (vs), 1433 (s), 1326 (m), 1265 (w), 1155 (w), 1101 (s), 1047 (vs), 989 (w), 969 (vs), 855 (m), 780 (s), 754 (vs), 690 (m) **Raman** (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3277(1), 3184 (14), 2761 (8), 2093 (5), 2062 (6), 1692 (4), 1580 (5), 1450 (9), 1327 (4), 1274 (74), 1159 (6), 1100 (100), 1046 (57), 990 (10), 970 (49), 787 (62), 552 (12). **^{1}H NMR** (DMSO-d_6, 25 °C, ppm): δ = 11.73 (s, 6 H); **^{13}C{^{1}H} NMR** (DMSO-d_6, 25 °C, ppm): δ = 154.9); **EA** (CH_6N_6O, 118.1): calcd.: C 10.17, H 5.12, N 71.16 %; found: C 10.55, H 4.83, N 71.06 %; **BAM drophammer**: > 40 J; **friction tester**: > 252 N; **ESD**: > 1.5 J.

Hydroxylammonium-5-oxotetrazolate·NH_3O (8)

Tetrazolone (860 mg, 10 mmol) was dissolved in hot water (20 mL) and 50 % Hydroxylamine in water (1.320 g) was added. The solution was left for crystallization. Big, colorless plates were collected from the beaker yielding 1.37 g (90 %) of product. **DSC** (5 K min^{-1}): 138 °C (dec). **^{1}H NMR** (DMSO-d_6 25 °C, ppm): δ = 8.15 (s); **^{13}C{^{1}H} NMR** (DMSO-d_6 25 °C, ppm): δ = 158.8. **IR** (atr, cm^{-1}): $\tilde{\nu}$ = 3225 (s), 1605 (vs), 1450 (m), 1423 (m), 1328 (w), 1270 (w), 1151 (w), 1051 (w), 981 (w), 771 (w), 739 (w); **Raman** (1064 nm, 200 mW, 25 °C (cm^{-1})): $\tilde{\nu}$ = 2930 (43), 2693 (46), 1643 (7), 1542 (8), 1437 (16), 1353 (10), 1280 (100), 1156 (11), 1101 (88), 1066 (84), 1005 (85), 776 (11), 525 (9); **BAM drophammer**: > 40 J; **friction tester**: 324 N; **ESD**: 0.4 J.

Symbols and Abbreviations

D	Detonation Velocity/m s^{-1}
δ	Chemical shift/ppm
$\Delta_f H$	Heat of formation/kJ mol^{-1}
$\Delta_f U$	Energy of formation/kJ kg^{-1}
$\Delta_E U^\circ$	Energy of explosion/kJ kg^{-1}
EA	Elemental analysis
ESD	Electrostatic discharge/J
FS	Friction sensitivity/N
FW	Formula weight/g mol^{-1}
H_2O	Water
IS	Impact sensitivity/N
N	Nitrogen content/%
NMR	Nuclear magnetic resonance
Ω	Oxygen balance/%
p_{CJ}	Detonation pressure/Pa
PETN	Nitropenta
RDX	Hexogen
T_{dec}	Decomposition Temperature/°C
T_E	Explosion Temperature/°C

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Energetic materials based on 3,5-diamino-1-nitroguanidine

Dennis Fischer*, Thomas M. Klapötke and Jörg Stierstorfer

Energetic Materials Research, Department of Chemistry,
University of Munich (LMU), Butenandtstr. 5-13, D-81377, Germany

dfich@cup.uni-muenchen.de

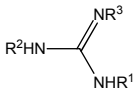
Abstract:

*3,5-Diamino-1-nitroguanidine (**DANQ**) was synthesized for the first time. The five step protocol starts with the reaction of CS_2, NH_3 and Me_2SO_4. DANQ was characterized by low temperature X-ray diffraction, Raman and IR spectroscopy, NMR spectroscopy, mass spectrometry, and differential scanning calorimetry. The energetic properties (heat of formation, sensitivities, theoretical detonation parameters) are investigated and compared to those of its prominent mother compound nitroguanidine. **DANQ** can be easily protonated by mineralic or organic acids which was confirmed by the ionic derivatives diamino-nitroguanidinium chloride (**DANQ_Cl**) and diamino-nitroguanidinium 2-oxido-5-nitrotetrazolate (**DANQ_NTX**). Diazotation of **DANQ** was carried out in various media obtaining the desired energetic compounds 1-amino-5-nitriminotetrazole (**AHATNO$_2$**) and 3,6-dinitramino-1,2,4,5-tetrazine (**DNAT**). In addition one ionic derivative of **AHATNO$_2$** the hydroxylammonium 1-amino-5-nitriminotetrazolate (**HxAATNO$_2$**) has been synthesized and characterized exemplarily. The performance parameters of all energetic compounds were calculated with the EXPLO5.05 computer code based on quantum chemical calculated heats of formation (CBS-4M based) and X-ray densities.*

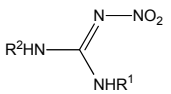
Keywords:Explosives; Guanidines; Nitroguanidines; Crystal Structure; Heat of Formation

1 Introduction

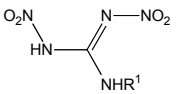
Guanidine chemistry has extended over a period of more than 100 years, and many useful compounds have been identified. The spectrum of uses of these compounds is highly diverse, ranging from biologically active molecules to highly energetic materials, thus indicating the manifold usability of the guanidine moiety as building block. Prominent inorganic candidates of guanidine are depicted in Figure 1. The relatively strong bases guanidine [1], 1-aminoguanidine [2], 1,3-diaminoguanidine, and 1,3,5-triaminoguanidine have often been described in literature mostly used in their protonated forms in high-nitrogen inorganic salts. Mononitrated nitroguanidine (NQ) [3] can be found in many applications, e.g. (i) in pyrotechnic compositions (ii) double based propellants (formulated with nitrocellulose (NC)) (iii) triple based propellants (NQ + NC + other HEDM (e.g. hexogen)) or (iv) as insecticide. It is easily obtained by nitration of guanidinium sulfate or nitrate. Its aminated analogue amino-nitroguanidine (ANG) is less described in literature. The structure of ANQ and protonated energetic salts was recently investigated in our group.[4] Also the ANQ halogenides and the sulfate has been described recently.[5] Up to now, the double aminated compound diamino-nitroguanidine (DANQ), which is in the focus of this study has never been described yet. The twice nitrated dinitroguanidine (DNQ) has intensively studied in the literature in its neutral as well as deprotonated form. 5-Amino-1,3-dinitroguanidine has never been described yet.



Guanidine, G: R^1,R^2,R^3 = H
1-Aminoguanidine, AG: R^1= NH_2; R^2,R^3 = H
1,3-Diaminoguanidine, DAG: R^1,R^2= NH_2; R^3 = H
1,3,5-Triaminoguanidine, TAG: R^1,R^2,R^3 = NH_2



1-Nitroguanidine, NQ: R^1,R^2 = H
3-Amino-1-nitroguanidine, ANQ: R^1 = NH_2; R^2 = H
3,5-Diamino-1-nitroguanidine, DANQ: R^1,R^2 = NH_2

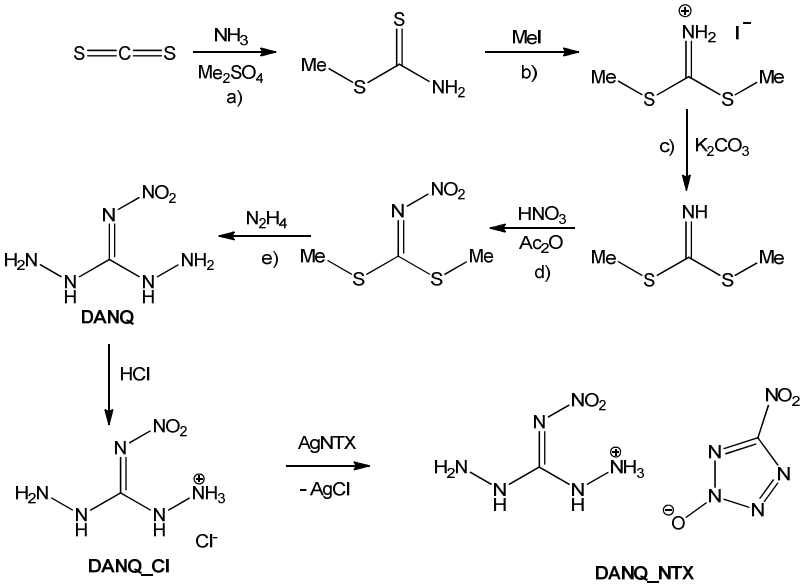


1,3-Dinitroguanidine, DNQ: R^1= H
(5-Amino-1,3-dinitroguanidine, ADNQ: R^1= NH_2)
(1,3,5-Trinitroguanidine, TNQ: R^1= NO_2)

Figure 1: Prominent inorganic guanidine derivatives containing $–NH_2$ and $–NO_2$ substituents.

2 Results and Discussion

ANQ is synthesized by the addition of **NQ** with an excess of hydrazine in methanolic solution.[6] A bigger excess of hydrazine, higher temperatures and longer reaction times do not yield **DANQ**. Therefore **DANQ** was synthesized by a different synthetic pathway shown in Scheme 1.



Scheme 1 Synthetic protocol of the formation of DANQ, DANQ_Cl and DANQ_NTX. Reaction conditions: a: THF, 2 h, RT; b: CH_3CN, 24 h, RT; c: Et_2O/H_2O, 0 °C; d) –5-5 °C, 1.5 h; e) MeOH, 0-20 °C, 5 h.

In the first reaction of the five step synthetic procedure ammonia was added to CS_2 which was then methylated using dimethyl sulfate forming S-methyl dithiocarbamate.[7] In the second step it was methylated with methyl iodide yielding the S,S´-dimethylcarbamate iodide [8], from which the free base was isolated using potassium carbonate. Nitration using 100% nitric acid and acetic anhydride yielded the N-nitro-S,S´dimethyldithiocarbamate [9] which was reacted with hydrazine hydrate in methanol forming crude **DANQ** which was dissolved in 2 M HCl to yield the pure hydrochloride in 30 % yield. **DANQ** is barely stable in neutral or basic solution. It decomposes in water, but a small amount of crystals were obtained from an almost completely evaporated aqueous solution by quickly washing away the decomposition products with cold water.

The structure of the crystalline state at 173 K was determined using X-ray diffraction. All X-ray measurement and solution parameters are collected in Table 1. The structure of the molecular moiety is shown in Figure 2. It crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The calculated density of 1.735 g cm^{-3} is marginal lower in comparison to **ANQ** (1.767 g cm^{-3}) [4] and **NQ** (1.78 g cm^{-3}) [10]. The molecular structure of **DANQ** is similar to that observed for **ANQ**. With respect to the non-hydrogen atoms the molecule is nearly planar. The nitro group is slightly twisted out of the plane (< C1–N1–N2–O1 – 6.24(16)°). Two intramolecular hydrogen bonds with the ring graph sets [11] R(1,1)5, and R(1,1)6 are observed for N5–H5···N4 and N3–H3···O1, respectively. All C–N bond lengths as well as the N1–N2 bond length are between single and double bonds. Both hydrazine N–N bond lengths are similar (ca. 1.41 A) and in the range of typical N–N single bonds.

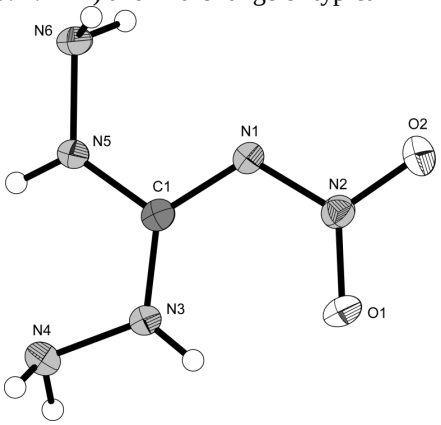


Figure 2: Molecular unit of **DANQ** determined by XRD. Ellipsoids of non-hydrogen atoms represent 50% probability. Selected bond distances [Å]: O1–N2 1.2492(13), O2–N2 1.2408(13), N1–N2 1.3369(13), N1–C1 1.3684(15), N3–C1 1.3273(16), N3–N4 1.4140(15), N5–C1 1.3323(16), N5–N6 1.4134(14); selected bond angles [°]: N2–N1–C1 118.39(9), O2–N2–O1 120.94(10), O2–N2–N1 115.18(9), O1–N2–N1 123.88(9), C1–N3–N4 117.30(11), C1–N5–N6 124.65(10).

Single crystals of diamino-nitroguanidinium chloride were obtained by recrystallizing the crude **DANQ** from 2 M HCl. The compound crystallizes in the monoclinic space group $P2_1/c$ with a density of 1.811 g cm^{-3}. The molecular moiety is shown in Figure 3. Interestingly, protonation of nitrogen N4 does not influence the structure details of the cations, so that the bond lengths and angles are similar to those observed for neutral **DANQ**.

In order to investigate an energetic salt of **DANQ**, its chloride was reacted with a solution of silver 2-oxido-5-nitrotetrazolat.[12] The obtained diamino-nitroguanidinium 2-oxido-5-nitrotetrazolate crystallized anhydrous from water and the crystal structure was also determined by low temperature XRD. The molecular moiety is shown in Figure 3. The salt crystallizes in the orthorhombic space group *Pbca* with eight anion/cation pairs in the unit cell. The density of 1.776 g cm^{-3} is similar to that of neutral **DANQ**.

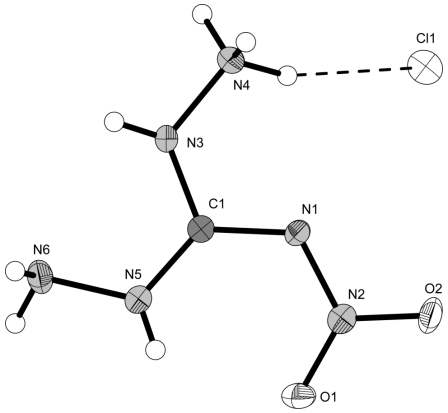


Figure 3: Diamond plot of DANQ_Cl. Ellipsoids of non-hydrogen atoms represent 50% probability. Selected bond distances of the cation [Å]: O1–N2 1.2427(19), O2–N2 1.2361(19), N1–N2 1.349(2), N1–C1 1.354(2), N3–C1 1.348(2), N3–N4 1.415(2), N5–C1 1.315(2), N5–N6 1.416(2); selected bond angles of the cation [°]: N2–N1–C1 118.95(14), O2–N2–O1 122.13(14), O2–N2–N1 114.53(14), O1–N2–N1 123.34(14), C1–N3–N4 119.63(15), C1–N5–N6 118.85(16).

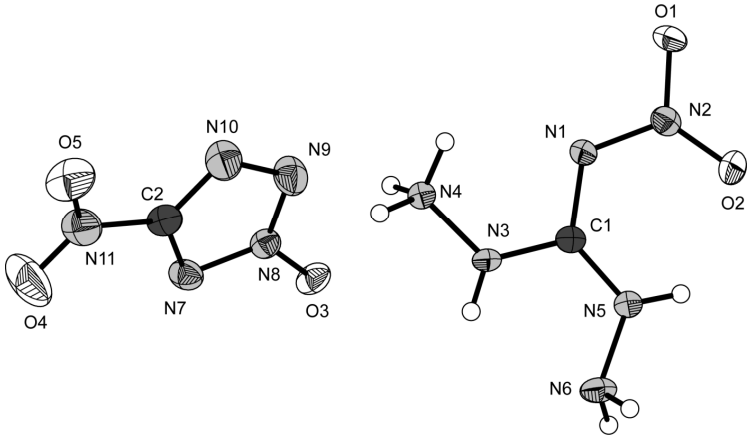


Figure 4: Diamond plot of **DANQ_NTX**. Ellipsoids of non-hydrogen atoms represent 50% probability. Selected bond distances of the cation [Å]: O1–N2 1.2494(14), O2–N2 1.2361(14), N1–N2 1.3384(16), N1–C1 1.3570(17), N3–C1 1.3382(18), N3–N4 1.4130(16), N5–C1 1.3142(18), N5–N6 1.4128(17); selected bond angles of the cation [°]: N2–N1–C1 118.71(11), O2–N2–O1 121.97(11), O2–N2–N1 124.43(12), O1–N2–N1 113.60(11), C1–N3–N4 117.30(11), C1–N5–N6 124.65(10).

The low yield of **DANQ_Cl** implies the formation of various side products. One of the side products crystallized during the recrystallization of the crude **DANQ**. 3-Nitrimino-6-thiomethyl-1,2,5-trihydro-1,2,4,5-tetrazine **(NATMT)** crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$. The asymmetric unit consist of two different molecules, one of them shown in Figure 5. The trihydro-tetrazine ring is not planar (e.g. torsion angle N1–N2–C2–N4 39.4(3)°) and shows cis-arrangement. The compound must have formed via the nucleophilic attack of **DANQ** to N-nitro-S,S´dimethyldithiocarbamate with nitramine and thiomethanol leaving as depicted in Scheme 2.

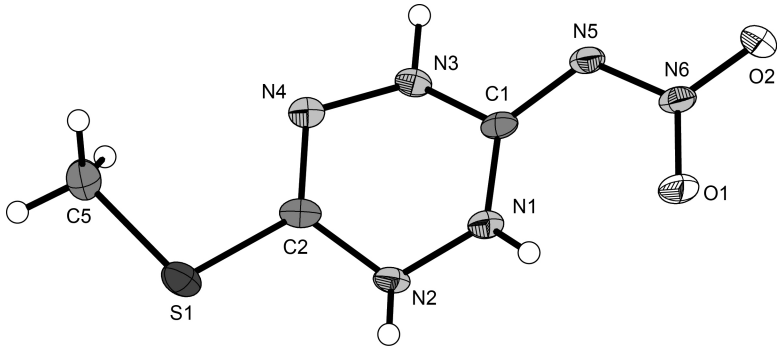
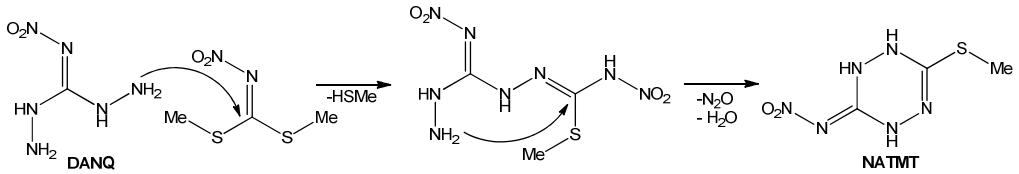
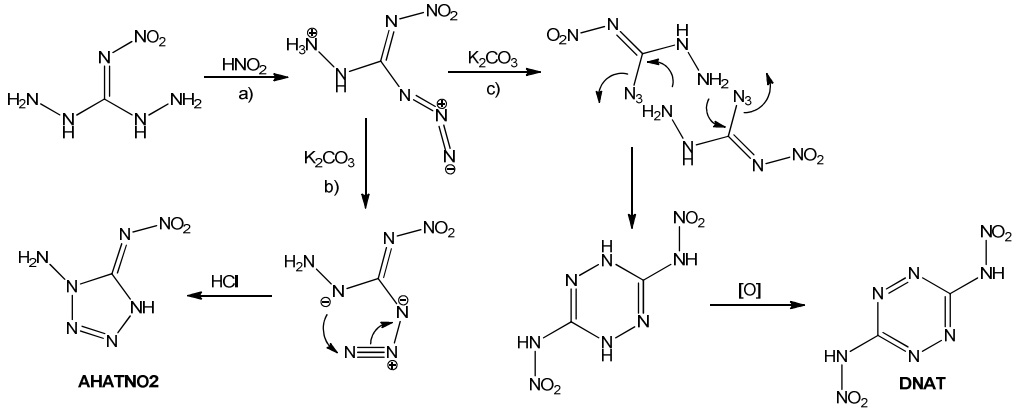


Figure 5: Molecular structure of 3-nitrimino-6-thiomethyl-1,2,5-trihydro-1,2,4,5-tetrazine. Ellipsoids of non-hydrogen atoms represent 50% probability. Selected bond length [Å]: S1–C2 1.733(3), S1–C5 1.809(3), O1–N6 1.258(3), O2–N6 1.237(3), N1–C1 1.319(3), N1–N2 1.429(3), N2–C2 1.404(4), N3–C1 1.355(3), N3–N4 1.427(3), N4–C2 1.289(3), N5–N6 1.347(3), N5–C1 1.355(3); selected bond angles [°]: C2–S1–C5 100.27(14), C1–N1–N2 116.3(2), 122(2), C2–N2–N1 111.3(2), C1–N3–N4 120.1(2), C2–N4–N3 112.0(2), N6–N5–C1 117.9(2), O2–N6–O1 121.8(2), O2–N6–N5 116.3(2), O1–N6–N5 121.9(2), N1–C1–N3 115.2(2), N1–C1–N5 130.0(3), N3–C1–N5 114.7(2), N4–C2–N2 120.6(3), N4–C2–S1 124.4(2), N2–C2–S1 114.78(18).

The synthesis of the energetic compound 3,6-dinitramino-1,2,4,5-tetrazine (**DNAT**) has been a long-time goal for the "energetic" community. However, numerous attempts to nitrate 3,6-diaminotetrazine failed. Chavez reported about the nitration of diamino-1,2,4,5-tetrazine forming **DNAT** but he claimed it to be very sensitive towards moisture and being hydrolized to the starting material.[13] We finally obtained **DNAT** via diazotation of **DANQ** as depicted in Scheme 3. The compound crystallized from the organic phase after diazotation of **DANQ** followed by treatment with K_2CO_3 , acidification and extraction into ethylacetate. If Chavez is right, **DNAT** must have formed via the oxidation of the colourless dihydro derivative by oxygen in the organic phase after drying.



Scheme 2 Mechanism of the formation of **NATMT**



Scheme 3 Synthetic protocol and mechanism of the formation of **AHATNO$_2$** and **DNAT**. Reaction conditions: a: 2 M HCl, 0 °C, 5 min; b: 0° C 10 min; c: 30 °C, 30 min.

DNAT crystallizes in the orthorhombic space group *Pbca* with four molecules in the unit cell. The density of 1.909 g cm^{-3} is much higher in comparison to 3,6-diaminotetrazine (1.611 g cm^{-3}) published in the literature.[14] The tetrazine ring together with the nitrogen atoms N3 form a planar backbone. The nitro groups are twisted out of the ring plane (torsion angle N1–C1–N3–N4 60.81(19)°). The proton connected to N3 forms a strong hydrogen bond to the nitrogen atom N1^{ii}. (N3–H3···N1^{ii}, 0.844(17) Å, 2.074(17) Å, 2.9170(18) Å,177.7(19)°), (ii) 0.5+x, 0.5–y, 1–z.

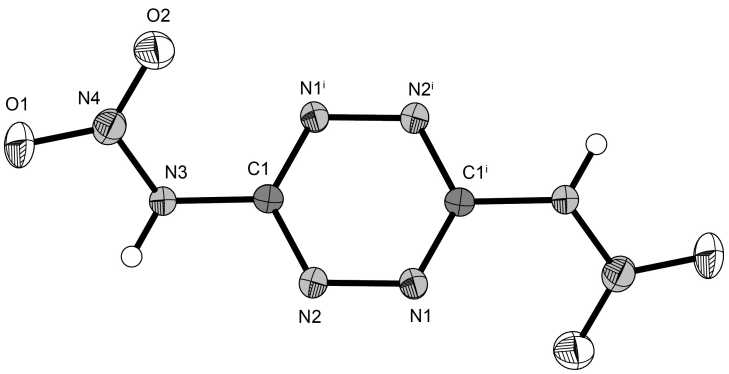


Figure 6: Molecular structure of 3,6-dinitramino-1,2,4,5-tetrazine (**DNAT**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å): O1–N4 1.2203(18), N2–C1 1.340(2), O2–N4 1.2190(18), N3–N4 1.382(2), N1–N2 1.3216(19), N3–C1 1.391(2), N1–C1^{ii} 1.3343(19); (i) –x, –y, 1–z

The synthesis of 1-amino-5-nitriminotetrazole (**AHATNO$_2$**) has been a mission in our research group for a long time. The nitration of 1,5-diaminotetrazole and protected derivatives has been researched recently.[15] However, we could not obtain **AHATNO$_2$** by these routes. **AHATNO$_2$** forms also during diazotation of **DANQ** followed by treatment with K_2CO_3 according to Scheme 2. The difference to the formation of **DNAT** is that here the diazotation time of **DANQ** is very short and that the reaction was treated with K_2CO_3 in the cold before it

was acidified and extracted with ethyl acetate. Single crystals of **AHATNO$_2$** were obtained from the organic phase. It crystallizes in the monoclinic space group $P2_1/c$ with eight molecules in the unit cell. One molecule of the asymmetric unit has been depicted in Figure 7. Its density of 1.777 g cm^{-3} is lower than that of not aminated derivative 5-nitriminotetrazole (1.867 g cm^{-3}) and comparable to that of 1-methyl-5-nitriminotetrazole (1.755 g cm^{-3}).[16]

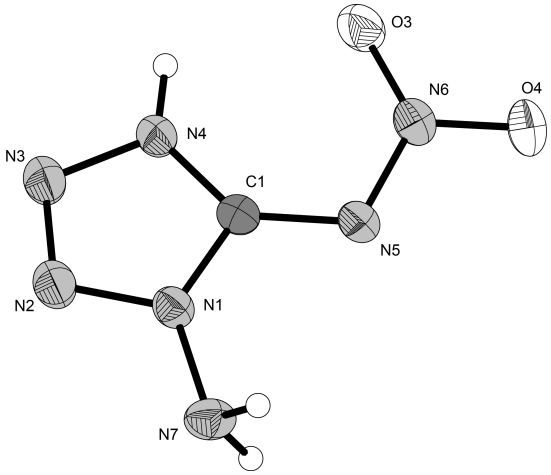


Figure 7: Molecular structure of 1-amino-5-nitriminotetrazole (**AHATNO$_2$**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å): O3–N6 1.2410(14), O4–N6 1.2532(14), N1–C1 1.3409(16), N1–N2 1.3543(16), N1–N7 1.3921(16), N2–N3 1.2761(16), N3–N4 1.3571(16), N4–C1 1.3288(17), N5–N6 1.3336(15), N5–C1 1.3453(17); selected bond angles [°]: C1–N1–N2 110.32(11), C1–N1–N7 130.06(11), N2–N1–N7 119.45(11), N3–N2–N1 107.51(11), N2–N3–N4 107.97(11), C1–N4–N3 110.30(11), N6–N5–C1 114.48(11), O3–N6–O4 121.38(11), O3–N6–N5 123.47(11), O4–N6–N5 115.14(11), N4–C1–N1 103.90(11), N4–C1–N5 136.44(12), N1–C1–N5 119.58(12).

Numerous nitrogen-rich salts of 1-amino-5-nitriminotetrazole were synthesized. Exemplarily, the hydroxylammonium salt (**Hx_AATNO$_2$**) is presented here. Its molecular structure is shown in Figure 8. **Hx_AATNO$_2$** crystallizes in the triclinic crystal system with two anion/cation pairs in the unit cell. Interestingly its density of 1.836 g cm^{-3} is higher than that observed for the neutral compound but in agreement to other hydroxylammonium tetrazolates described in the literature.[17]

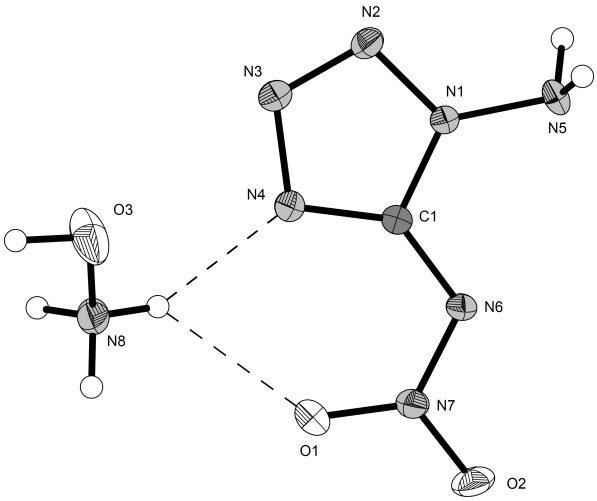


Figure 8: Molecular moiety of hydroxylammonium 1-amino-5-nitriminotetrazolate (**HxANAT**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å): O1–N7 1.2420(18), O2–N7 1.2492(17), N1–C1 1.350(2), N1–N2 1.3508(18), N1–N5 1.3907(18), N2–N3 1.2943(18), N3–N4 1.3680(19), N4–C1 1.336(2), N6–N7 1.3262(18), N6–C1 1.360(2), N8–O3 1.4035(19); selected bond angles [°]:C1–N1–N2 109.53(13), C1–N1–N5 126.27(13), N2–N1–N5 124.18(13), N3–N2–N1 105.87(12), N2–N3–N4 111.46(12), C1–N4–N3 105.76(12), N7–N6–C1 117.28(13), O1–N7–O2 120.87(13), O1–N7–N6 123.25(13), O2–N7–N6 115.83(12), N4–C1–N1 107.37(13), N4–C1–N6 134.48(14), N1–C1–N6 118.09(13).

Table 1: X-ray data and parameters

	DANQ	**DANQ_Cl**	**DANQ_NTX**	**NATMT**
Formula	$CH_6N_6O_2$	$CH_7N_6O_2Cl$	$C_2H_{12}N_{11}O_5$	$C_3H_6N_6O_2S$
M [g mol^{-1}]	134.12	170.58	265.19	190.21
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space Group	$P2_1/c$	$P2_1/c$	$Pbca$	$Pna2_1$
Color / Habit	Colorless rod	Colorless rod	Colorless block	Colorless block
Size [mm]	0.15 x 0.18 x 0.20	0.08 x 0.15 x 0.24	0.15 x 0.18 x 0.30	0.21 x 0.30 x 0.38
a [Å]	3.5786(2)	6.5095(3)	10.9606(7) 8.5601(5)	18.4385(10)
b [Å]	14.4056(8)	12.0210(5)	21.2619(13)	3.8554(2) 20.6218(15)
c [Å]	10.0412(6)	8.0484(4)	90	90
α [°]	90	90	90	90
β [°]	97.393(5)	96.494(4)	90	90
γ [°]	90	90		
V [Å^3]	513.34(5)	625.75(5)	1994.9(2)	1465.96(15)
Z	4	4	8	8
$\rho_{calc.}$ [g cm^{-3}]	1.735	1.811	1.766	1.724
μ [mm^{-1}]	0.154	0.560	0.163	0.411
F(000)	280	352	1088	784
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173	173	173	173
θ range [°]	4.3, 26.5	4.2, 26.0	4.2, 26.0	4.4, 26.0
Dataset (h; k; l)	–4:4; –18:18; –12:12	–8:7; –10:14; –9:7	–12:13; –10:10; –26:23	–21:22; –3:4; –25:23
Reflect. coll.	7528	3126	9703	6960

Independ. refl.	1069	1210	1960	2690
R_{int}	0.026	0.019	0.033	0.035
Reflection obs.	866	1022	1465	2499
No. parameters	106	119	191	265
R_1 (obs)	0.0275	0.0259	0.0289	0.0304
wR_2 (all data)	0.0776	0.0764	0.0728	0.0684
S	1.08	1.11	0.94	1.05
Resd. Dens. [e Å^{-3}]	–0.23, 0.16	–0.21, 0.31	–0.19, 0.17	–0.19, 0.26
Device type	Oxford Xcalibur3 CCD [18]	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92 [19]	SIR-97	SIR-92	SIR-92
Refinement	SHELXL-97 [20]	SHELXL-97	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan [21]	multi-scan	multi-scan	multi-scan

Table 2: X-ray data and parameters

	DNAT	**AHATNO$_2$**	**Hx_AATNO$_2$**
Formula	$C_2H_2N_8O_4$	$CH_3N_7O_2$	$CH_6N_8O_3$
M [g mol^{-1}]	202.12	145.10	178.14
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space Group	*Pbca*	$P2_1/n$	*P*–1
Color / Habit	orange block	Colorless rod	Colorless block
Size [mm]	0.23 x 0.27 x 0.32	0.13 x 0.15 x 0.20	0.18 x 0.20 x 0.22
a [Å]	9.3988(7)	8.6799(4)	7.3527(13)
b [Å]	7.8812(6)	8.6486(4)	7.3659(12)
c [Å]	9.4936(8)	14.8777(7)	7.4706(15)
α [°]	90	90	110.155(17)
β [°]	90	103.810(5)	103.871(16)
γ [°]	90	90	111.113(16)
V [Å^3]	703.23(10)	1084.57(9)	322.30(14)
Z	4	8	2
$\rho_{calc.}$ [g cm^{-3}]	1.909	1.777	1.836
μ [mm^{-1}]	0.177	0.159	0.167
F(000)	408	592	184
$\lambda_{MoK\alpha}$ [Å]	0.71073	0.71073	0.71073
T [K]	173	173	173
θ range [°]	4.3, 26.0	4.7, 26.0	4.9, 26.5
Dataset (h; k; l)	–9:11; –9:8; –11:11	–10:10; –10:10; –18:18	–9:9; –9:9; –9:9
Reflect. coll.	3279	10581	3407
Independ. refl.	684	2124	1340
R_{int}	0.030	0.027	0.030
Reflection obs.	535	1587	1104
No. parameters	68	205	133
R_1 (obs)	0.0339	0.0267	0.0376
wR_2 (all data)	0.0922	0.0693	0.0987
S	1.04	0.94	1.08
Resd. Dens. [e Å^{-3}]	–0.27, 0.22	–0.15, 0.18	–0.29, 0.46
Device type	Oxford Xcalibur3 CCD [18]	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	SIR-92 [19]	SIR-92	SIR-92
Refinement	SHELXL-97 [20]	SHELXL-97	SHELXL-97
Absorpt. corr.	multi-scan [21]	multi-scan	multi-scan

^{13}C NMR spectroscopy of **DANQ** in DMSO-d_6 yielded one signal at 161.0 ppm. In the ^{1}H NMR spectrum two broad signals were obtained at 9.36 and 4.43 ppm. In the ^{14}N NMR spectrum only the nitro resonance could be detected at –14.6 ppm. The thermal behavior determined by differential scanning calorimetry (DSC (heating rate 5 deg min^{-1}) showed decomposition above 136 °C. The ^{13}C NMR resonance of **AHATNO$_2$** shows up one signal at 149.2 ppm. In the ^{1}H NMR spectrum only one broad signal at 8.02 ppm could be observed due to the acidic nature of the proton located at the ring. **AHATNO$_2$** decomposes above 145 °C with a heating rate of 5 deg min^{-1}.

In order to compare the energetic properties to those of **NQ** and **ANQ** the heats of formation have been calculated theoretically by the atomization method based on CBS-4M electronic energies, which have been shown suitable in different currently published papers.[22,23] A comparison of the gas phase enthalpies of all guanidine derivatives mentioned in Figure 1 are listed in Table 3.

The detonation parameters were calculated using the program EXPLO5 V5.05.[24] The calculations was performed using the maximum densities according to the crystal structures. Heats of formation were computed theoretically. All calculations were carried out using the Gaussian G09 program package.[25] The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied the modified CBS-4M method (**M** referring to the use of Minimal Population localization) which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections. The enthalpies of the gas-phase species M (Table 2) were computed according to the atomization energy method (eq. 1).

$$\Delta_f H°_{(g,\,M,\,298)} = H_{(Molecule,\,298)} - \sum H°_{(Atoms,\,298)} + \sum \Delta_f H°_{(Atoms,\,298)} \qquad (1)$$

Using calculated heat of sublimation for **1** by the *Trouton's* Rule [26] and lattice enthalpies for the ionic compounds the gas-phase enthalpies of formation were converted into the solid state (standard conditions) enthalpy of formation $\Delta_f H_m°$ (Table 3). Lattice energies (U_L) and lattice enthalpies (ΔH_L) were calculated from the corresponding molecular volumes according to *Jenkin's* equations.[27]

Table 3: Gas phase enthalpies of formation of guanidine derivatives and their protonated forms based on CBS-4M electronic energies and the atomization method.

Compound	Sum formula	E / H°	Δ_fH(g) / kJ mol^{-1}
DANQ / H$^+$DANQ	$CH_6N_6O_2$ / $CH_7N_6O_2^+$	–519.842471 / 520.166175	284.7 / 968.7
ANG / H$^+$ANG	$CH_5N_5O_2$ / $CH_6N_5O_2^+$	–464.602726 / 464,914496	161.7 / 877.0
NG / H$^+$NG	$CH_4N_4O_2$ / $CH_5N_4O_2^+$	–409.357802 / 409.693035	52.4 / 706.0
G / H$^+$G	CH_5N_3 / $CH_6N_3^+$	–205.075149 / 205.453192	30.7 / 571.9
AG / H$^+$AG	CH_6N_4 / $CH_7N_4^+$	–260.323872 / 260.701802	130.1 / 671.6
DAG / H$^+$AG	CH_7N_5 / $CH_8N_5^+$	–315.562810 / 315.949896	255.2 / 750.2
TAG / H$^+$TAG	CH_8N_6 / $CH_9N_6^+$	–370.792867 / 371,197775	403.7 / 874.3
DNG / H$^+$DNG*	$CH_3N_5O_4$	–613.620392	126.7

E: Electronic energy; Δ_fH(g): Gas phase enthalpy of formation.; * not known yet.

Several detonation parameters are shown in Table 4 in comparison to RDX. All compounds have detonation velocities above 9000 m/s and detonation pressures ranging from 341 to 419 kbar. $AHATNO_2$ and Hx_AATNO_2 were tested for sensitivities using BAM methods. $AHATNO_2$ has an impact sensitivity of 2 J and a friction sensitivity of 5 N. Hx_AATNO_2 has an impact sensitivity of 3 J and a friction sensitivity of 10 N and therefore both compounds are powerful but also sensitive explosives.

Table 4: Energetic and detonation parameters of the energetic compounds described in this work.

	DANQ	**DANQ_NTX**	**DNAT**	**AHAT-NO_2**	**Hx_AATNO$_2$**	**RDX**
Formula	$CH_6N_6O_2$	$C_2H_7N_{11}O_5$	$C_2H_2N_8O_4$	$CH_3N_7O_2$	$CH_6N_8O_3$	$C_3H_6N_6O_7$
FW / g mol^{-1}	134.10	265.15	202.09	145.08	178.11	222.12
N / %	62.67	58.11	55.45	67.58	62.91	37.8
Ω / %	–35.79	–15.08	–7.92	–16.54	–29.61	–21.6
$T_{Dec.}$ / °C	136	90	120 (est.)	145		210
ρ / g cm^{-3}	1.735	1.766	1.909	1.777	1.836	1.80
$\Delta_f H_m°$ / kJ mol^{-1}	208.0	618.6	534.1	440.6	458.4	70
$\Delta_f U°$ / kJ kg^{-1}	1680.1	2440.2	2728.1	3139.0	2691.3	417
EXPLO5.04 values:						
$-\Delta_{Ex}U°$ / kJ kg^{-1}	5463	6614	6673	6221	5818	6125
T_{det} / K	3516	4559	5047	4532	3801	4236
P_{CJ} / kbar	341	373	419	368	398	349
$V_{Det.}$ / m s^{-1}	9122	9211	9340	9170	9589	8748
V_o / L kg^{-1}	892	817	715	807	875	739

3 Conclusions

From this experimental study the following conclusions can be drawn: Diaminonitroguanidine (DANQ) was synthesized for the first time from N-nitro-S,S´dimethyldithiocarbamate and hydrazine. DANQ itself is not stable in aqueous solution but it can be protonated to form salts which are more stable. DANQ was diazotized with nitrous acid yielding 1-amino-5-nitriminotetrazole and 3,6-dinitramino-1,2,5,6.tetrazine, respectively, depending on the reaction conditions. 1-Amino5-nitriminotetrazole and its hydroxylammonium salt are powerful but sensitive explosives.

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PAPER

Pushing the limits of energetic materials – the synthesis and characterization of dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate†

Niko Fischer, Dennis Fischer, Thomas M. Klapötke,* Davin G. Piercey and Jörg Stierstorfer

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The safe preparation and characterization (XRD, NMR and vibrational spectroscopy, DSC, mass spectrometry, sensitivities) of a new explosive dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50) that outperforms all other commonly used explosive materials is detailed. While much publicized high-performing explosives, such as octanitrocubane and CL-20, have been at the forefront of public awareness, this compound differs in that it is simple and cheap to prepare from commonly available chemicals. TKX-50 expands upon the newly exploited field of tetrazole oxide chemistry to produce a material that not only is easily prepared and exceedingly powerful, but also possesses the required thermal insensitivity, low toxicity, and safety of handling to replace the most commonly used military explosive, RDX (1,3,5-trinitro-1,3,5-triazacyclohexane). In addition, the crystal structures of the intermediates 5,5′-bistetrazole-1,1′-diol dihydrate, 5,5′-bistetrazole-1,1′-diol dimethanolate and dimethylammonium 5,5′-bistetrazole-1,1′-diolate were determined and presented.

Introduction

The rational design of new energetic materials is a rapidly exploding field[1–7] with a long traditional rooting in the chemical sciences[8,9] and a complexity that rivals that of the drug design. While the field has come a long way since the days of Liebig, Berzelius and Gay-Lussac, and the concept of isomerism being determined from explosive silver fulminate and non-explosive silver cyanate,[10] current work in this field still follows the trend of its historic beginnings; that of simultaneous academic and practical interest and advances. In the quest for higher-performing, safer, cheaper, greener, explosive materials, energetic materials chemistry must push the boundaries of the energy capacity of compounds, which requires new classes of compounds,[2,11] new synthetic strategies,[12] and advanced computational techniques. For example, the high nitrogen content of many advanced explosives has led to the preparation of new nitrogen–nitrogen bond forming reactions[12] and new heterocyclic systems[13] in the quest for even higher performance.

In both civilian and military circles, the highest performing explosives make use of the same strategy: cyclic and caged nitramines. Belonging to the oldest class of explosives, those derive their energy from the oxidation of a carbon backbone by containing the oxidizer in the same molecule; RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaza-isowurtzitane) all have fatal flaws that mandate replacement with modern explosives. Advanced energetic strategies allow for retention or improvement of the explosive performance, while avoiding the multitude of downsides present in these compounds: toxicity to living organisms (all), difficult and expensive synthesis (HMX, CL-20), high sensitivity to mechanical stimuli (all), and spontaneous changing of properties (CL-20).[2] New strategies in the design of energetic materials include those with ring or cage strain, high heat of formation compounds, and compounds containing strong dipoles or zwitterionic structures.[14]

Unfortunately, the known materials with the highest detonation energy are often highly sensitive due to their unprecedented energy content,[5] and are made *via* long and expensive pathways with a multitude of steps, making industrial scale-up infeasible. For example, both DDF (dinitroazofuroxane) and ONC (octanitrocubane) possess detonation velocities at the limit of known performances (around 10 000 m s^{-1}), however both are highly

Energetic Materials Research, Department of Chemistry, University of Munich (LMU), Butenandtstr. 5-13, D-81377, Germany. E-mail: tmk@cup.uni-muenchen.de; Fax: +49 (0)89 2180 77492; Tel: +49 (0)89 2180 77491

† Electronic supplementary information (ESI) available: 1. Materials and methods; 1.1. NMR spectroscopy; 1.2. vibrational spectroscopy; 1.3. mass spectrometry and elemental analysis; 1.4. differential scanning calorimetry; 1.5. sensitivity testing; 2. experimental work; 2.1. synthesis *via* oxidation of 5,5′-bistetrazole with potassium peroxymonosulfate; 2.2. synthesis *via* cyclization of diazidoglyoxime; 2.3. safer synthesis including a multi-step one pot reaction; 3. X-ray diffraction; 3.1. instrument and refinement software; 3.2. crystallographic data and refinement parameters; 3.3. bond lengths, bond angles and hydrogen bonding of TKX-50; 3.4 crystal structures of 5,5′-bistetrazole-1,1′diol; 3.5. crystal structure of dimethylammonium 5,5′-bistetrazole-1,1′diolate; 4. explosive performance; 4.1. heat of formation calculations; 4.2. small scale shock reactivity test; 4.3 flame test; 4.4 hot plate test; 5. toxicity assessment; 6. Fast Cook-Off test. cif files. CCDC 872230, 872231, 872232, 884559, 884560 and 884561. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2jm33646d

sensitive and have more than 10 synthetic steps with exotic, expensive reagents used.[15]

A very promising explosophoric moiety in the design of new energetic materials is the tetrazole ring; the carbon on position 5 of the ring allows the facile attachment of various substituents for energetic tailorability, and the high nitrogen content and heat of formation of the heterocycle lead to high energetic performances. In order to improve the energetic properties of tetrazoles, several recently published studies showed that introduction of N-oxides yields compounds with even higher densities and stabilities, lower sensitivities and better oxygen balances.[2,7,11] Combining these principles with practical considerations in mind, a simple and secure synthetic pathway to the high performing energetic material dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate (TKX-50) was devised.

Results and discussion

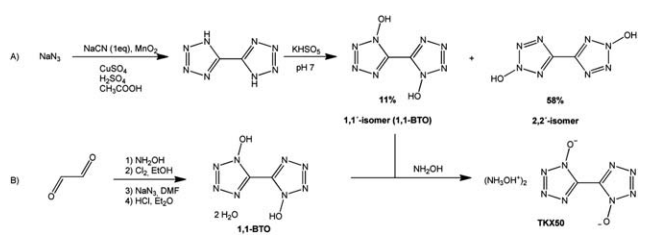
Synthesis (simple and scalable)

There are two major routes (A and B) to the 5,5′-bistetrazole-1,1′-diol (1,1-BTO) moiety (Scheme 1). The first (A) of which, the oxidation of the parent heterocycle with aqueous potassium peroxymonosulfate only leads to 1,1-BTO in poor yield (11%). The oxidation of the 5,5′-bistetrazolate anion with peroxymonosulfate was carried out in a manner similar to that we have previously reported for 5-nitro- and 5-azidotetrazoles.[2,7] Unfortunately, this reaction was found to produce the 2,2′ isomer as the major product, with only traces of the 1,1′ isomer which crystallized upon adding aqueous hydroxylamine.

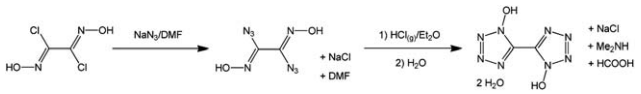
After discovering the outstanding characteristics of TKX-50 as a high explosive, a different route to the precursor 5,5′-bistetrazole-1,1′-diol was necessitated. Tselinskii *et al.*[16] reported on the synthesis of the mentioned precursor 1,1-BTO from the cyclization of diazidoglyoxime under acidic conditions for the first time. Diazidoglyoxime is prepared from dichloroglyoxime in a chloro–azido exchange reaction in DMF with more than 80 % yield, whereas dichloroglyoxime is prepared from glyoxime *via* chlorination in ethanol in high yield.

The problematic step here is the isolation of the highly friction and impact sensitive compound diazidoglyoxime, mandating a revised procedure before industrial-scaled use. The problem was overcome by a procedure combining the formation and cyclization of diazidoglyoxime in one step in solution. Starting from commercially available glyoxal, the reaction process was transformed into a five step, four pot synthesis to isolate TKX-50.

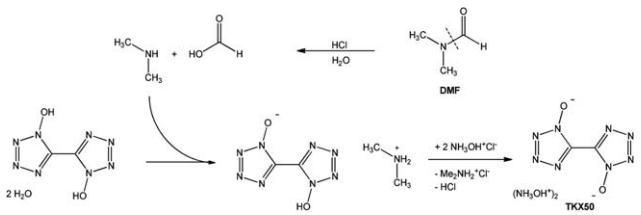
The prepared solution of diazidoglyoxime in DMF (impure with sodium chloride) is directly poured into diethylether and



Scheme 1 Synthesis of TKX-50 *via* oxidation of 5,5′-bistetrazole (A) and *via* cyclization of diazidoglyoxime (B).



Scheme 2 Synthesis of 5,5′-bistetrazole-1,1′-diol in a one pot reaction from dichlororglyoxime.



Scheme 3 Synthesis of TKX-50 from 5,5′-bistetrazole-1,1′-diole isolated from the one pot reaction described in Scheme 2. DMF is cleaved under the acidic conditions to form the dimethylammonium salt of 5,5′-bistetrazole-1,1′-diol, which is then converted into TKX-50.

HCl gas is bubbled through (Scheme 2). After cyclization of the azidooxime in the acidic medium the dimethylammonium salt of 5,5′-bistetrazole-1,1′-diol is formed by a reaction with dimethylamine (formed by hydrolysis of DMF). After isolation and recrystallization of dimethylammonium 5,5′-bistetrazole-1,1′-diolate, it is dissolved in a sufficient amount of boiling water and combined with a solution of hydroxylammonium chloride, from which TKX-50 crystallizes first (Scheme 3).

An alternative procedure using NMP (*N*-methyl-2-pyrrolidone) instead of DMF for the chloro–azido exchange, followed by the same treatment, leads to the free acid 5,5′-bistetrazole-1,1′-diol which is then isolated as its sodium salt tetrahydrate upon the addition of aqueous sodium hydroxide and subsequently treated with hydroxylammonium chloride in water. Starting from dichloroglyoxime, the overall yields of both procedures are very high with 72 % (DMF-route) and 85 % (NMP-route) for the synthesis of TKX-50. For a detailed description of all synthetic routes yielding TKX-50 and for all analytical data please refer to the ESI.†

X-ray diffraction

The crystal structure of TKX-50 was determined at three temperatures (100 K, 173 K, 298 K) in order to detect potential low temperature phase transitions and obtain precise densities (for explosive performance calculations). In addition the crystal structures of the intermediates 5,5′-bistetrazole-1,1′-diol dihydrate (recryst. from either water, MeCN, EtOH or glacial acetic acid), 5,5′-bistetrazole-1,1′-diol dimethanolate (recryst. from methanol) and dimethylammonium 5,5′-bistetrazole-1,1′-diolate (crystallized from H_2O) were determined and are presented in the ESI.† Detailed crystallographic data and parameters of the measurements and solutions are given in Table S1.† The lack of observed phase transitions between 100 K and 298 K is advantageous for energetic materials use as constant properties upon temperature changes result. The density follows the expected trend of decreasing with increased temperature (100 K: 1.918 g cm^{-3} > 173 K: 1.915 g cm^{-3} > 298 K: 1.877 g cm^{-3}). TKX-50 crystallizes in the monoclinic space group $P2_1/c$ with two anion–cation moieties in the unit cell. The molecular moiety of

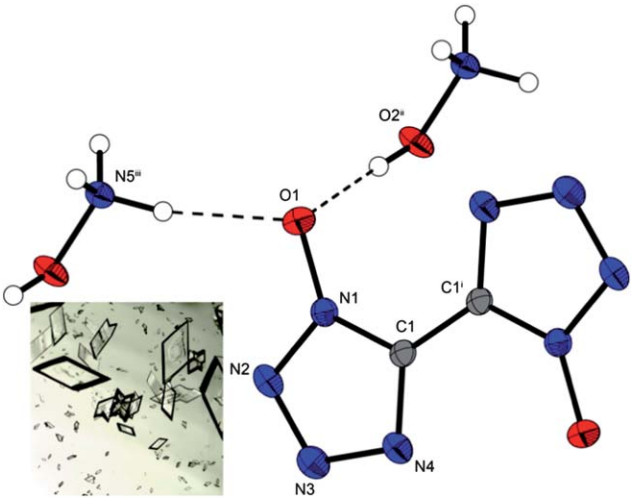


Fig. 1 Representation of the solid state molecular structure of TKX-50 at 100 K. Thermal ellipsoids are drawn at the 50% probability level; symmetry codes: (i) $2 - x, -y, 2 - z$; (ii) $x, 0.5 - y, -0.5 + z$; and (iii) $-1 + x, 0.5 - y, -0.5 + z$.

TKX-50 at 100 K is depicted in Fig. S1.† Its density of 1.918 g cm^{-3} is significantly higher than that of non-oxide dihydroxylammonium 5,5′-bistetrazolate (1.742 g cm^{-3}) recently published.[17] The reason for this may be the strong hydrogen bond network (involving all four hydrogen atoms of the hydroxylammonium cations) (Fig. 1).

Energetic performance

The performance data (Table 1) were calculated with the computer code EXPLO5.05 (latest version). EXPLO5.05 is based on the chemical equilibrium, a steady state model of detonation. It uses Becker–Kistiakowsky–Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's equation of state for solid carbon (see ESI†). The input is based on the sum formula, calculated heats of formation (see ESI†) and the maximum densities according to their crystal structures (ESI, Table S1†).

With respect to the detonation velocity (Table 1), TKX-50 shows higher calculated values than all other mass-produced and used explosives like 2,4,6-trinitrotoluene (TNT), RDX, HMX and CL-20. Looking at the detonation pressure, TKX-50 exceeds the values calculated for TNT and RDX and is comparable to HMX, but is slightly lower than for CL-20. Also in terms of potential use as a propellant mixture ingredient TKX-50 shows promising values due to its high nitrogen content. The calculated specific impulse using 60 bar isobaric rocket conditions is 261 seconds, which is slightly better than those of the other compounds in Table 1.

To assess the explosive performance of TKX-50 on a small laboratory scale, a small-scale reactivity test (SSRT) was carried out (see ESI†) in comparison to CL-20 and RDX. Here, a defined volume of the explosive is pressed into a perforated steel block, which is topped with a commercially available detonator (Orica, DYNADET-C2-0ms). Initiation of the tested explosive results in denting a separate aluminium block, which is placed right underneath the steel block (Fig. 2). From measuring the volumes of the dents (CL-20 ≥ TKX-50 ≫ RDX) (Table 2 in the ESI†), it can be concluded that the small scale explosive performance of TKX-50 exceeds the performance of commonly used RDX and is comparable to that of CL-20.

The performance and safety characteristics for shipping of an explosive can be related to the data obtained from the Koenen test.[18,19] The explosive is placed in an open-ended, flanged steel tube, which is locked up with a closing plate with variable orifice (0–10 mm), through which gaseous decomposition products are

Table 1 Energetic properties and detonation parameters of prominent high explosives in comparison to TKX-50

	2,4,6-TNT	RDX	β-HMX	ε-CL-20	TKX-50
Formula	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$	$C_2H_8N_{10}O_4$
Molecular mass [g mol^{-1}]	227.13	222.12	296.16	438.19	236.15
IS [J][a]	15 [21]	7.5 [21]	7 [21]	4 [21]	20
FS [N][b]	353	120 [21]	112 [21]	48 [21]	120
ESD-test [J][c]	—	0.20	0.20	0.13	0.10
N [%][d]	18.50	37.84	37.84	38.3	59.3
Ω [%][e]	−73.96	−21.61	−21.61	−10.95	−27.10
T_m [°C][f]	81	205 [22]	275 [24]	—	—
$T_{dec.}$ [°C][f]	290	210 [24]	279 [24]	215 [23]	221
Density [g cm^{-3}][g]	1.713 (100 K)[24] 1.648 (298 K)[25]	1.858 (90 K)[26] 1.806 (298 K)[27]	1.944 (100 K)[28] 1.904 (298 K)[28]	2.083 (100 K)[29] 2.035 (298 K)[29]	1.918 (100 K)[30] 1.877 (298 K)[30]
Theor. $\Delta_f H°$ [kJ mol^{-1}][h]	−55.5	86.3	116.1	365.4	446.6
Theor. $\Delta_f U°$ [kJ kg^{-1}][i]	−168.0	489.0	492.5	918.7	2006.4
EXPLO5.05 values					
$-\Delta_E U°$ [kJ kg^{-1}][j]	5258	6190	6185	6406	6025
T_E [K][k]	3663	4232	4185	4616	3954
p_{C-J} [kbar][l]	235	380	415	467	424
D [m s^{-1}][m]	7459	8983	9221	9455	9698
Gas vol. [L kg^{-1}][n]	569	734	729	666	846
I_S [s][o]	205	258	258	251	261

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance ($\Omega = (xO - 2yC - 1/2zH)M/1600$). [f] Decomposition temperature from DSC ($\beta = 5$ °C min^{-1}). [g] From X-ray diffraction. [h] Calculated (CBS-4M method) enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products). [o] Specific impulse using isobaric (60 bar) conditions.

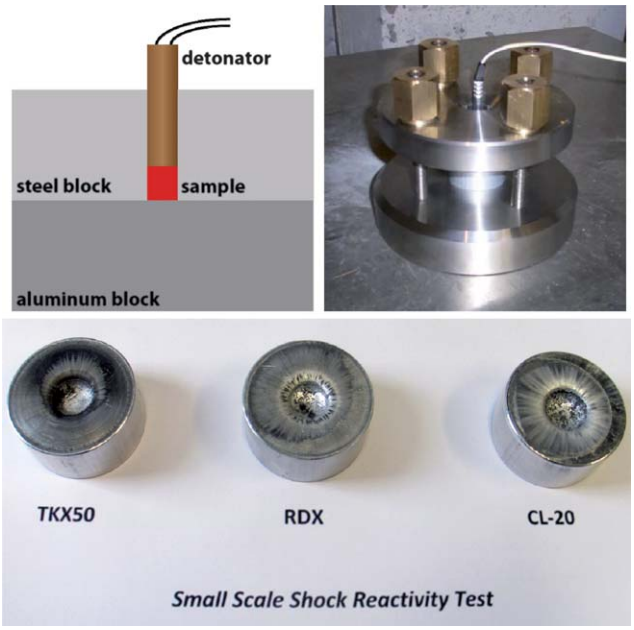


Fig. 2 Small-scale reactivity test of TKX-50, RDX and CL-20. Above pictures: test setup for the SSRT. Below: dented aluminium blocks after initiation of the explosive with a commercial detonator.

vented. A defined volume of 25 mL of the compound is loaded into the flanged steel tube and a threaded collar is slipped onto the tube from below. The closing plate is fitted over the flanged tube and secured with a nut. The decomposition is initiated *via* thermal ignition using four Bunsen burners, which are ignited simultaneously. The test is completed when either rupture of the tube or no reaction is observed after heating the tube for a minimal time period of at least 5 min. In the case of the tube's rupture, the fragments are collected and weighed. The reaction is evaluated as an explosion if the tube is destroyed into three or more pieces. The Koenen test was performed with 23.0 g of TKX-50 using a closing plate with an orifice of 10 mm and caused the rupture of the steel tube into approximately 100 pieces, the size of which reached down to smaller than 1 mm from 40 mm (Fig. 3).

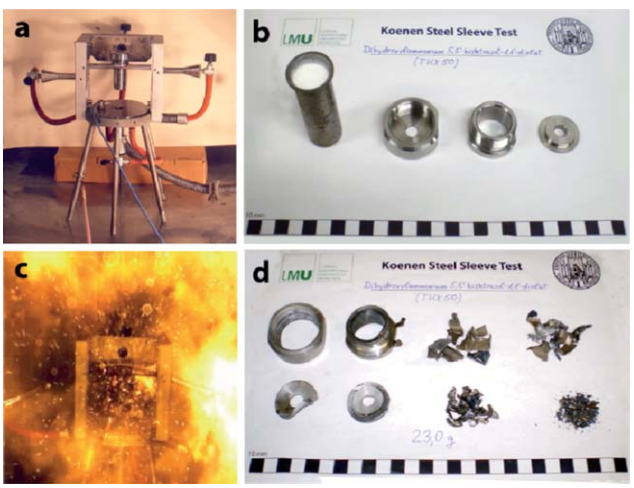


Fig. 3 a) Koenen test experimental setup. (b) Parts of the Koenen steel sleeve before and (d) after the test. (c) Moment of detonation.

TNT destroys the steel tube up to an orifice width of 6 mm, RDX even up to 8 mm.[20] In order to get an "Interim Hazard Classification" also a "Fast Cook-Off test" (UN test 3d) was performed in which TKX-50 underwent controlled deflagration (no explosion occurred).

High safety – low sensitivity

Impact sensitivity is a high priority in explosive devices used in the military due to the range of stresses devices may be exposed to. The impact sensitivity of TKX-50 is 20 J which is much lower than those for RDX, HMX and CL-20, which range from 4 to 7.5 J, and all three of which need desensitizing components added for practical use. The low impact sensitivity of TKX-50 shows that it can be used without desensitization.

Friction sensitivity is more important in the manufacturing context, where TKX-50 with 120 N is of comparable or lower sensitivity than any of RDX, HMX or CL-20, increasing the margin of safety in the industrial context. Both the impact and friction sensitivities of TKX-50 as compared to 2,4,6-trinitrotoluene (TNT), RDX, HMX and CL-20 are presented in Table 1.

The human body can generate up to 25 mJ of static electricity, which can easily set off the most sensitive explosives such as lead azide or silver fulminate. TKX-50 has an electrostatic sensitivity of 0.100 J, which is far higher than the human body can generate, allowing a comparable margin of safety when handling, comparable to RDX or HMX.

Thermal stability is important for any explosive in practical use as demanding military requirements need explosives that can withstand high temperatures. For example, a munition sitting in the desert can exceed 100 °C and for general use a component explosive must be stable above 200 °C. TKX-50 with a decomposition onset of 222 °C easily surpasses this requirement (Fig. 4, inset). This stability has been confirmed using a long-term stability test, where the sample is heated in an open glass vessel to a temperature of 75 °C over 48 h to ensure safe handling of the material even at elevated temperatures (Fig. 4, outer curve). The lack of exothermic or endothermic events in the sample temperature or heat flow curve implies that the compound is stable.

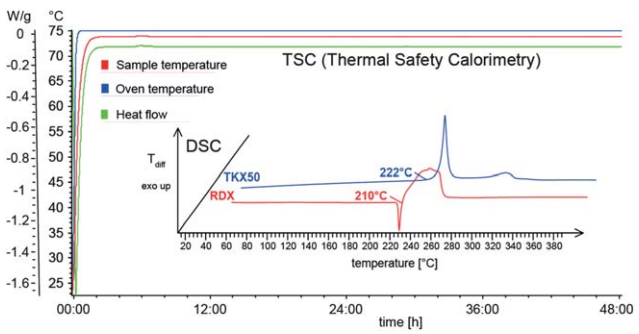


Fig. 4 Outer curve: long term stability (TSC plot) of TKX-50 at a temperature of 75 °C over a period of 48 h. Inner plot: thermal stability of TKX-50 and RDX shown in the DSC plot (heating rate 5 °C min^{-1}).

Toxicity – environmentally friendly

One of the major aims in our search for new "green" energetic materials is the low toxicity of the newly investigated compound

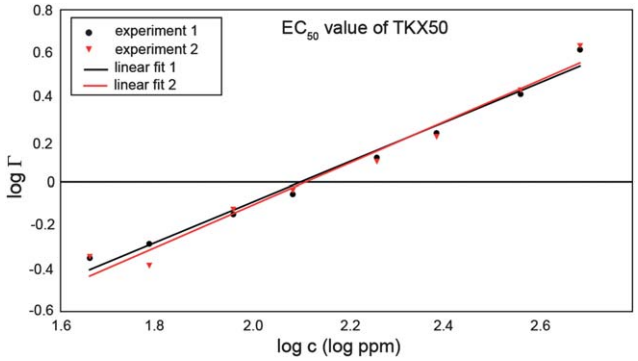


Fig. 5 Toxicity assessment of TKX-50 using a luminescent bacteria inhibition test. Plot of log Γ against log c for determination of the EC_{50} value.

itself, and of its degradation and decomposition products. In recent times the toxicity of energetic materials is a growing concern due to new understandings of the fate of explosives in the environment. The nitramine content of the ubiquitous RDX as well as less used HMX and CL-20 has been shown to be toxic to vital organisms at the base of the food chain, and in addition RDX is a probable human carcinogen. To assess the toxicity of TKX-50 to aquatic life, diluted aqueous solutions of the high explosive were subjected to the luminescent marine bacterium *Vibrio fischeri* using the commercially available bioassay system LUMIStox®. *Vibrio fischeri* is a representative species for other aquatic life and therefore a useful indicator when it comes to groundwater pollution. Being the most important toxicological parameter, the EC_{50} value of the sample was determined. EC_{50} is the effective concentration of the examined compound, at which the bioluminescence of the strain *Vibrio fischeri* is decreased by 50% after a defined period of exposure as compared to the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound. For RDX we observe an EC_{50} value of 91 ppm after an incubation time of 30 minutes. The herein determined EC_{50} value of TKX-50 of 130 ppm (Fig. 5 and ESI†) lies significantly above the EC_{50} value found for RDX indicating a lower toxicity to *Vibrio fischeri*, and as such, other aquatic life.

Conclusions

We have detailed the preparation of a new explosive, TKX-50 or dihydroxylammonium 5,5′-bistetrazole-1,1′-diolate. This material has exemplified the utility of the tetrazole N-oxide chemistry by providing a new explosive material that is of very high performance (as calculated and demonstrated by SSRT testing), pushing the limits towards the most powerful explosives known, and synthesized in an industrially viable process. Additionally, TKX-50 is of lower sensitivity (mechanically and thermally) than its contemporaries in currently used explosives such as RDX, HMX and CL-20, making increased margins of safety when applied in practical use and devices. Finally, we have demonstrated the lower toxicity of TKX-50 compared to the nitramine RDX, as determined by the EC_{50} value for the decrease in luminescence of *Vibrio fischeri*. All of the characteristics of TKX-50 make it appropriate and exemplary to not just fulfill the long-standing goal of a "green" RDX replacement, but also to replace it with a material of superior performance.

Acknowledgements

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Synthesis of 5-Aminotetrazole-1*N*-oxide and Its Azo Derivative: A Key Step in the Development of New Energetic Materials

Dennis Fischer, Thomas M. Klapötke,* Davin G. Piercey, and Jörg Stierstorfer[a]

Abstract: 1-Hydroxy-5-aminotetrazole (**1**), which is a long-desired starting material for the synthesis of hundreds of new energetic materials, was synthesized for the first time by the reaction of aqueous hydroxylamine with cyanogen azide. The use of this unique precursor was demonstrated by the preparation of several energetic compounds with equal or higher performance than that of commonly used explosives, such as hexogen (RDX). The prepared compounds, including energetic salts of 1-hydroxy-5-aminotetrazole (hydroxylammonium (**2**, two polymorphs) and ammonium (**3**)), azo-coupled derivatives (potassium (**5**), hydroxylammonium (**6**), ammonium (**7**), and hydrazinium 5,5′-azo-bis(1-*N*-oxidotetrazolate (**8**, two polymorphs)), as well as neutral compounds 5,5′-azo-bis(1-oxidotetrazole) (**4**) and 5,5′-bis(1-oxidotetrazole)-hydrazine (**9**), were intensively characterized by low-temperature X-ray diffraction, IR, Raman, and multinuclear NMR spectroscopy, elemental analysis, and DSC. The calculated energetic performance, by using the EXPLO5 code, based on the calculated (CBS-4M) heats of formation and X-ray densities confirm the high energetic performance of tetrazole-*N*-oxides as energetic materials. Last but not least, their sensitivity towards impact, friction, and electrostatic discharge were explored. 5,5′-Azo-bis(1-*N*-oxidotetrazole) deflagrates close to the DDT (deflagration-to-detonation transition) faster than all compounds that have been investigated in our research group to date.

Keywords: azides · azo compounds · combustion · energetic materials · X-ray diffraction

Introduction

Within any field of scientific research, strategies for obtaining the desired results evolve over time as new insights and results become available; energetic materials, which encompass all propellants, explosives, and pyrotechnics, are no exception. From the early days of chemistry, when young Justus Liebig′s enthrallment with firecrackers at the local market sparked his interest in fulminates,[1,2] to the modern strategies of cage-strained[3] and high-nitrogen compounds,[4] various strategies have fallen in and out of favor for the design of new energetic materials. Recently, "hot" strategies in the design of high-performing energetic materials have fallen into two major categories, ring- or cage-strained compounds and compounds with high heats of formation, often in combination with the more traditional strategy of combining the fuel and the oxidizer in the same molecule.[5] Beyond the thrust for ever higher explosive or propellant performances, environmental considerations are becoming an ever more important aspect that is driving the development of these energetic materials. For example, the very high toxicity of fuel/oxidizer nitramine-derived cyclotrimethylenetrinitramine[6] (RDX) makes its replacement necessary.

Of the modern strategies for the design of explosive materials, nitrogen-rich, high-heat-of-formation materials have been shown to possess some of the most promising characteristics.[7–9] The energy content of these materials is derived from the unique characteristics of nitrogen species, whereby the N≡N triple bond is far more stable than its double- or single-bond analogues, thereby leading to a strong thermodynamic driving force towards the formation of nitrogen gas.[10–12] For energetic materials based on this strategy, a strong correlation between increasing heat of formation, increasing explosive performance, and, unfortunately, increasing sensitivity towards thermal and mechanical stimuli, can be observed. For example, when five-membered nitrogen heterocycles are compared, from pyrazole to pentazole, pyrazoles have very little energy content and pentazoles are not stable enough for use in energetic materials.[13] Of these heterocycles, the tetrazole ring has been found to occupy the ideal middle ground on the "stability versus performance continuum" for the preparation for new primary and secondary energetic materials. Of the energetic materials based on the tetrazole ring, a recurring theme is their preparation from 5-aminotetrazole; thus, this compound can act as a precursor for introducing the tetrazole ring synthon into a wide range of energetic materials.

The chemistry of aminotetrazole is very diverse, as can be seen from Scheme 1. Firstly, simple salt chemistry of 5-ami-

[a] D. Fischer, Prof. Dr. T. M. Klapötke, D. G. Piercey, Dr. J. Stierstorfer
Department of Chemistry, Energetic Materials Research
Ludwig Maximilian University
Butenandtstr. 5–13 (D), 81377 München (Germany)
Fax: (+49) 89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

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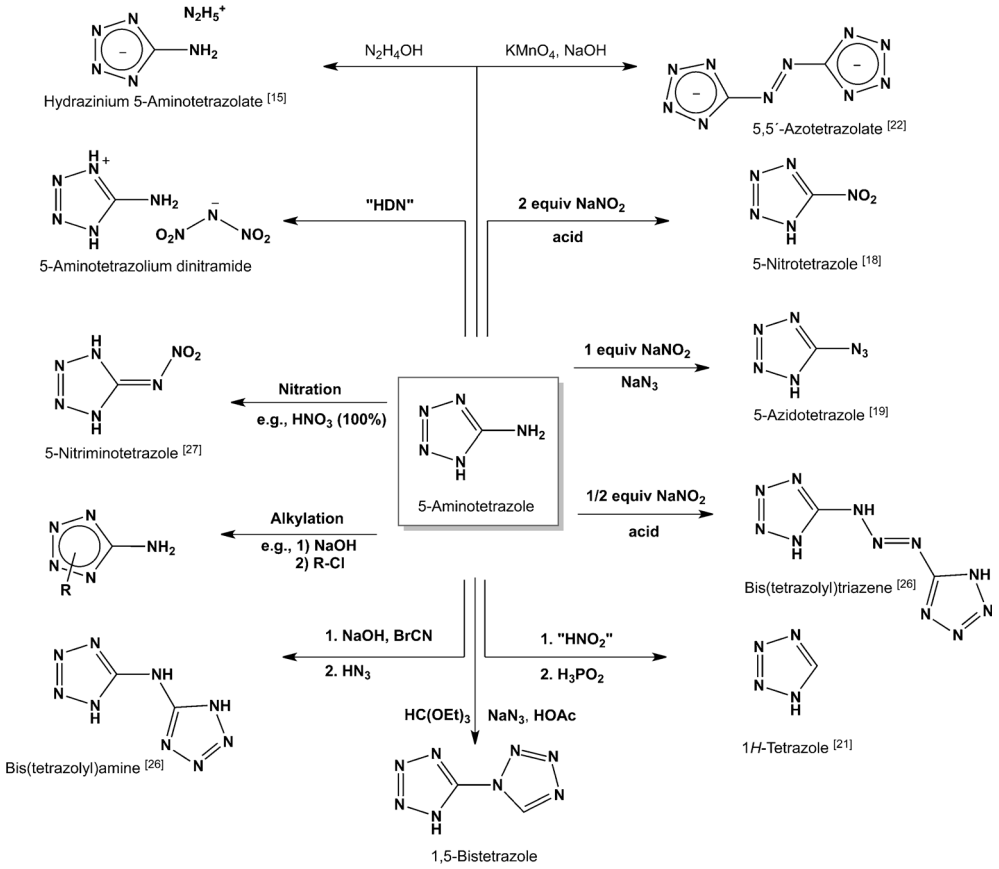


Scheme 1. Synthesis of selected energetic materials based on 5-aminotetrazole.

notetrazole has given such interesting compounds as hydrazinium aminotetrazolate,[14] which is a high-performance insensitive ingredient in explosives and propellants, whereas, on the more-sensitive side, disilver aminotetrazole perchlorate[15] is a useful and thermally stable primary explosive. When we consider the reactivity of the amino group, diazotization and subsequent substitution can lead to the 5-chloro, bromo,[16] nitro,[17] azido,[12,18] and -H tetrazoles,[20] of which copper(I) nitrotetrazolate is currently the most-promising replacement for lead azide,[19] as well as salts of 5H-tetrazole, which have found applications as colorants.[1,2] The amino group can also undergo azo coupling, thereby giving the 5,5′-azotetrazole[21] and, after reduction, 5,5′bistetrazolylhydrazine.[22] By reaction with various simple reagents, energetic triazines,[23] 1,5-bistetrazoles,[24] 5,5-bis(tetrazolyl)-amines,[25] and nitriminotetrazoles[26] are all available. Finally, the ring nitrogen atoms can be functionalized at either the 1- or 2-positions by using well-known amination[27] or alkylation reactions.[28] Within the field of energetic tetrazole chemistry, energetic compounds that are derived from 5-aminotetrazole and its derivatives likely make up the majority of these materials, as opposed to energetic tetrazoles that are derived from other precursors.

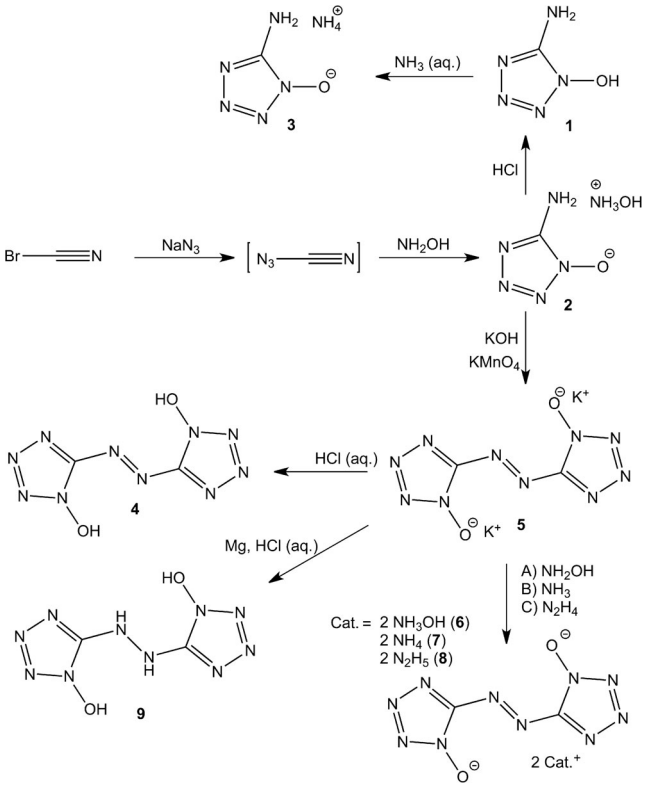
However, recently, a useful strategy for tailoring tetrazole-based energetic materials has involved the oxidation of the tetrazole rings into their corresponding tetrazole-*N*-oxides.[29,30] Many of the non-oxidized tetrazoles suffer from low oxygen balance and, beyond the improvement in their oxygen balance, in various systems, the N-oxides have shown both increased performance, increased thermal stability, and decreased mechanical sensitivity.[31–33] From our recent work in this field, tetrazole N-oxidation was found to increase both performance and density, whilst decreasing mechanical sensitivity; however, unfortunately, their thermal stability often decreased slightly. Despite this one drawback, tetrazole-*N*-oxides have been used to prepare TKX50, dihydroxylammonium bistetrazolate-1,1′-dioxide, a useful secondary explosive with performance exceeding that of HMX, one of the highest-performing military explosives in common use.[34]

However, a major limit of these tetrazole-*N*-oxides is that the available synthetic methods are not general in scope. The aqueous oxone oxidations that work for 5-nitro- or 5-azidotetrazoles fail on species such as 5-aminotetrazole, 5,5′-tetrazoletriazine, nitriminotetrazole, and bis(tetrazolyl)-amine, as a result of the presence of other oxidizable nitrogeneous species in the molecules. The other method, that is, the cyclization of azido–oximes, is also limited in both the scope of available azido–oximes and in the unfortunate property of very high sensitivity towards the manipulation of many azido–oximes. With the wide variety of energetic materials available from 5-aminotetrazole, a 5-aminotetra-

zole oxide would be ideal, thus allowing the preparation of the wide variety of energetic materials that are available from 5-aminotetrazole (Scheme 1), but with the proven advantages of the tetrazole-*N*-oxides.

1-Hydroxy-5-aminotetrazole (**1**) is readily and economically available from the reaction of aqueous hydroxylamine with cyanogen azide and we have synthesized several energetic materials from this unique precursor, including energetic salts of 1-hydroxy-5-aminotetrazole and its azo-coupled derivative, in an analogous manner to that of 5-aminotetrazole, thus giving 5,5′-azotetrazolate-1,1′-dioxide and its salts, energetic materials of very high performance. Recently, we described the synthesis and properties of 5,5′-azoxy-tetrazolates[35] and compared them to their azotetrazolates. Although not oxidized at the tetrazole ring, the N-oxide on the azo moiety improves the performance and stability of the azotetrazolate anion, which has found various applications, mainly in the energetic-materials sector, including use as gas-generating agents in propellant systems. For example, the bis(triaminoguanidinium) salt[36] has found application as a nitrogen-rich additive in the NILE (Navy Insensitive Low-Erosion) propellant.[37]

The prepared compounds were characterized by X-ray diffraction, IR, Raman, and multinuclear NMR spectroscopy, elemental analysis, and DSC. Their calculated energetic performance confirmed the highly energetic performance of tetrazole-*N*-oxides as energetic materials. Thus, the fields of energetic-materials chemistry and tetrazole-*N*-oxide chemistry is expanded by offering 1-hydroxy-5-aminotetrazole, which, when substituted in reactions in which 5-aminotetrazole is currently used, may potentially lead to hundreds of new energetic materials.



Scheme 2. Synthesis of 1-hydroxy-5-aminotetrazole (**1**), 1,1′-dihydroxy-5,5′-azobistetrazole (**4**), 1,1′-dihydroxy-5,5′-bistetrazolylhydrazine (**9**), and the salts thereof.

Results and Discussion

Synthesis: As depicted in Scheme 2, compound **1** is readily accessible from the reaction of a 50% aqueous solution of hydroxylamine with a solution of cyanogen azide in MeCN. If one equivalent of hydroxylamine is applied, pure compound **1** precipitates in a low yield (about 10%) from the MeCN solution. The yield can be increased to about 90% by using two equivalents of hydroxylamine, which precipitates the hydroxylammonium salt of 1-hydroxy-5-aminotetrazole (**2**) as a colorless powder. Because an unstable byproduct always formed by using this route, it was useful to cool the reaction medium down to −20°C before the addition step. The reaction is quite exothermic and leads to a temperature rise of 20°C at a concentration of cyanogen azide of 1.5%. The pure 50% aqueous solution of hydroxylamine (which contains no ammonia from autocatalytic decomposition) and the cooling process lead to a significant amount of pure product that is free from the unstable byproduct, which turns yellow on standing at room temperature and slowly decomposes into gaseous products. This unstable byproduct is probably another addition product of the reaction, because hydroxylamine can also attack through the oxygen atom. The presence of any open azides in the product can be excluded, owing to the absence of the azide vibration in the IR spectrum. Pure compound **1** can be obtained from the crude product by boiling it in an alkali solution of hydroxide to destroy the hydroxylamine and the as-yet-unknown byproduct, which turns bright red and decomposes in basic medium. After acidification, pure anhydrous HAT can be crystallized from the aqueous solution. The ammonium (**3**) and hydroxylammonium salts of compound **1** (**2**) were obtained from an aqueous solution of compound **1** after the addition of ammonia and 50% hydroxylamine, respectively.

Like 5-aminotetrazole, compound **1** can be azo-coupled by using permanganate in basic medium.[21] Because hydroxylamine and any other byproducts of the reaction are destroyed in hot basic media, the reaction can be carried out with crude compound **2**, thereby leading to an overall yield of approximately 60% relative to cyanogen bromide. The addition of one equivalent of potassium permanganate (1.5 redox equivalents) ensures complete coupling. Any excess manganese in any oxidation state above +4 is destroyed by the addition of MeOH. After the removal of MnO_2, the potassium salt of dihydroxyazotetrazole (K_2AzTO, **5**) can be crystallized as bright-red needle-shaped crystals. In contrast to its non-oxide derivative and also as recently described, azoxy-bis(tetrazole) azotetrazole dioxide does not decompose in acidic aqueous solution, thus con-

firming the stabilization by the hydroxyl moieties. The free dihydroxyazotetrazole (**4**) can be isolated as an orange solid by extraction into EtOAc and evaporation of the solvent. The color of the compound nicely reflects the effect of tetrazole N-oxidation. Whilst some colorless compounds, like 5-nitrotetrazole, become yellow upon oxidation,[29] the already yellow azotetrazole becomes orange and red, respectively, on the addition of an extra oxygen atom. The addition of ammonia, hydrazine, and hydroxylamine to solutions of the free acid leads to their corresponding salts.

Like azotetrazole, its oxide can be reduced into its hydrazine derivative and the reaction occurs without reducing the oxide.[22] An aqueous solution of compound **5** was boiled with magnesium powder until the solution became colorless. After removal of the magnesium, acidification, and extraction with EtOAc, a colorless solid remained. In basic medium in air, 1,1′-dihydroxy-5,5′-bistetrazolylhydrazine (BTHO, **9**) is quickly oxidized back into the azo compound like its non-oxide derivative and, therefore, working under an inert atmosphere is recommended for this reaction. In acidic medium, the compound is slowly oxidized by oxygen and the solid material stays mainly colorless.

Crystal structures: All of the compounds investigated herein were also characterized by low-temperature single-crystal X-ray diffraction. The data and parameters of the measurements and refinements are collected in the Supporting Information, Tables S1 and S2. Exact bond lengths and angles are also given in the Supporting Information, Tables S3 and S4.

1-Hydroxy-5-aminotetrazole (**1**) crystallizes in the monoclinic space group *Cc*. In contrast to the crystallographic determined 5-aminotetrazole monohydrate ($P2_1/c$, 1.502 g cm^{-3}),[38] compound **1** was obtained free from water with a significantly higher density (1.695 g cm^{-3}) that was also higher than that of the corresponding 1,5-diaminotetrazole (1.571 g cm^{-3});[39] this result nicely confirms the concept of increased density by N-oxide introduction. The structure of compound **1** is shown in Figure 1. All three hydrogen atoms participate in hydrogen bonds, thereby forming a wave-like layer structure along the *c* axis. Exact bond lengths and angles are provided in the Supporting Information, Table S3. When comparing the bond lengths of 5-aminotetrazole and compound **1**, interestingly, there are only marginally differences, mostly within the standard deviation. The bond lengths within the tetrazole rings are all between typical values for N–N and C–N single and N=N and C=N double bonds. In all of the investigated structures, the tetrazole rings are (almost) planar, including the N-oxide oxygen atom and the N5 nitrogen atom. In contrast to the structure of 5-aminotetrazole[38] and our investigated 1-oxido-5-aminotetrazolates, the NH_2 hydrogen atoms lie almost within the ring plane (N1–C1–N5–H51 = 7.5° in compound **1** versus 21.6° in compound **3**).

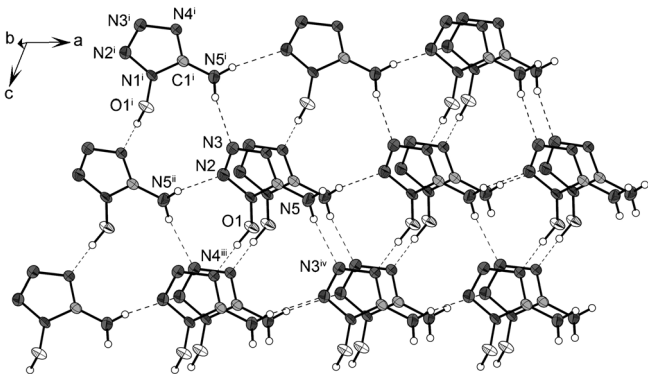


Figure 1. Crystal structure of compound **1**; ellipsoids are set at 50% probability. Hydrogen-bond lengths [A] and angles [°] (D–H···A, *d*(D–H), *d*(H···A), *d*(D···A), <(D–H···A)): N5–H51···N3^{i}: 0.88(4), 2.24(4), 3.106(4); 165(4). N5–H52···N2^{ii}: 0.83(4), 2.26(4), 3.076(4); 169(3). O1–H1···N4^{iii}: 1.01(6), 1.60(6), 2.609(3); 173(5). O1–H1···N3^{iii}: 1.01(6), 2.55(6), 3.477(3); 152(4). Symmetry codes: i) 0.5+*x*, 0.5−*y*, 0.5+*z*; ii) 0.5+*x*, 0.5+*y*, *z*; iii) *x*, 1−*y*, 0.5+*z*.

Hydroxylammonium 1-oxido-5-amino-tetrazolate (**2**) crystallizes in two different polymorphs, an orthorhombic one ($P2_12_12_1$, **2a**) with a density of 1.664 g cm^{-3} and a monoclinic one ($P2_1/c$, **2b**) with a higher density of 1.735 g cm^{-3}. The monoclinic form was obtained by crystallization from MeOH and the orthorhombic form from water. The original precipitate from MeCN was orthorhombic. The asymmetric unit of the low-density polymorph (**2a**) consists of two cation/anion pairs. The hydrogen bonds of one tetrazolate-*N*-oxide anion are shown in Figure 2 and Figure 3. The de-

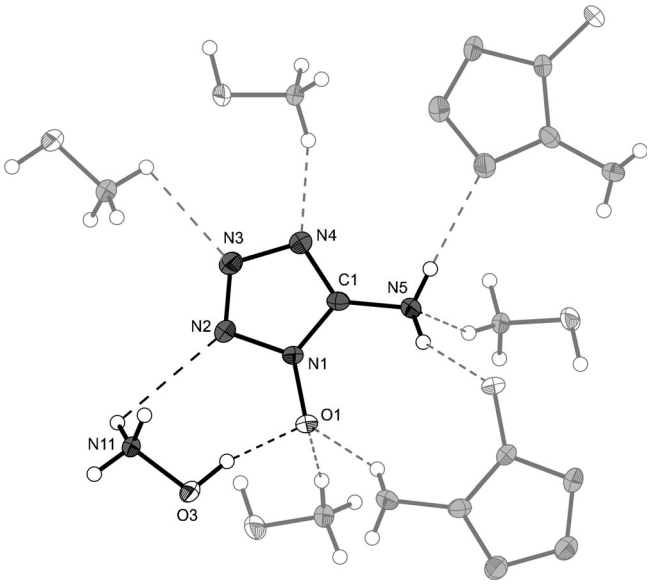


Figure 2. View of the molecular unit of compound **2a**, as well as of selected hydrogen bonds of one anion; ellipsoids are set at 50% probability.

protonation of compound **1** does not yield significant changes in the bond lengths of the anion. On average, the N-oxide N1–O1 and N3–N4 bond lengths are shortened by between 0.01 and 0.02 Å, whereas the N2–N3 distance is slightly elongated. The largest change is found in the C1–N5, distance which is elongated by about 0.03 Å.

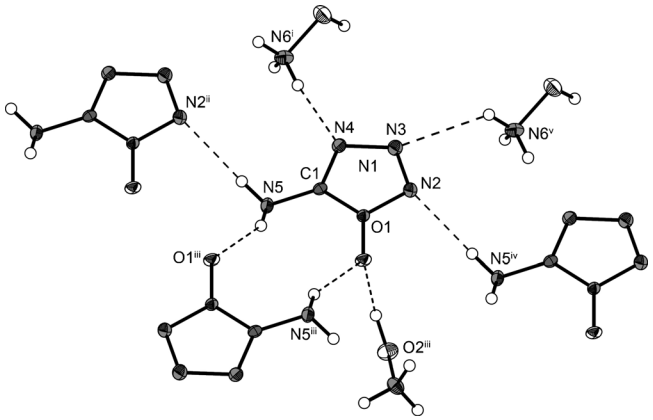


Figure 3. View of the hydrogen bonds of one tetrazolate anion in the structure of compound **2b**; ellipsoids are set at 50% probability. Symmetry codes: i) x, $0.5-y$, $-0.5+z$; ii) $1+x$, y, z; iii) $1-x$, $-y$, $-z$; iv) $-1+x$, y, z; v) $-1+x$, $0.5-y$, $-0.5+z$.

Ammonium 1-oxido-5-amino-tetrazolate (**3**) crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit consists of two cation/anion pairs. Although there are many strong hydrogen bonds that involve all of the protons on the ammonium cations (Figure 4), the density is only 1.530 g cm^{-3}, which is the lowest observed herein and also lower than that of comparable literature compounds, such as ammonium 5-azidotetrazolate (1.61 g cm^{-3})[12] and ammonium 5-nitrotetrazolate (1.64 g cm^{-3}).[40] The structure of the corresponding water-free ammonium 5-aminotetrazolate has not yet been reported.

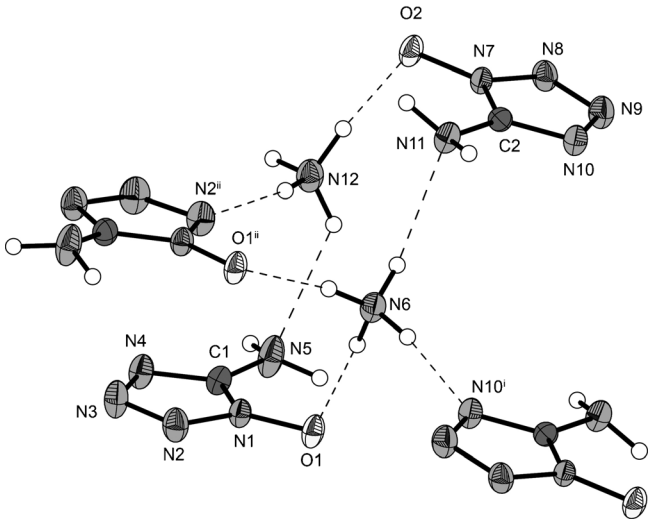


Figure 4. View of the coordination modes of the ammonium cations in the structure of compound **3**. Selected hydrogen bond lengths [A] and angles [°] (D–H···A, d(D–H), d(H···A), d(D···A), <(D–H···A)): N6–H6C···N: 110.91(2), 2.32(2), 3.163(2); 152.9(17). N6–H6D···N10^{i}: 0.93(2), 1.97(2), 2.894(2); 170.7(19). N6–H6B···O1: 0.95(3), 1.85(3), 2.763(2); 162(2). N6–H6A···O1^{ii}: 0.95(2), 1.85(2), 2.790(2); 171(2). Ellipsoids are set at 50% probability. Symmetry codes: i) $1-x$, $1-y$, $1-z$; ii) x, $1.5-y$, $-0.5+z$.

1,1′-Dihydroxy-5,5′-azotetrazole crystallizes in the monoclinic space group $P2_1/n$ with two molecules in the unit cell and a high density of 1.902 g cm^{-3}. The molecular unit is shown in Figure 5 A. Both tetrazole rings are coplanar (N1–C1–C1^{i}–N4^{i} = 2.9°), including the oxygen atoms. However, the hydrogen atoms are twisted out of the ring planes (N2–N1–O1–H1 = –29.6°), thereby forming the H-bond interactions shown in Figure 5 B.

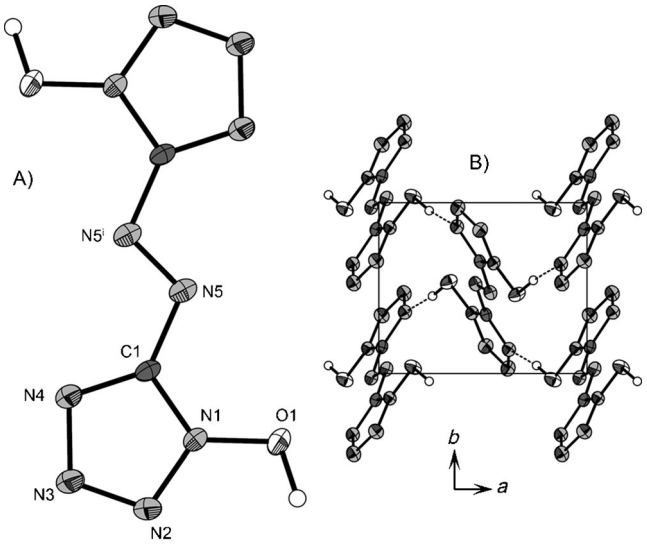


Figure 5. A) Molecular unit of compound **4**, which shows the labeling scheme; ellipsoids are set at 50% probability. Symmetry code: i) $2-x$, $-y$, $2-z$. B) View along the c axis, which shows the two different planes of the molecules that are connected by hydrogen bonds.

Potassium 5,5′-azo-bis(1-oxidotetrazolate) (**5**) crystallizes in the monoclinic space group $P2_1/c$ with two molecules in the unit cell and without the inclusion of crystalline water molecules. The calculated density of 2.20 g cm^{-3} cannot be compared to that of the corresponding dipotassium azotetrazolate[41] because it crystallizes with the inclusion of five crystal water molecules and tends to explode violently when dehydrated. The bond lengths of compound **5** are very similar to those observed for protonated compound **4**. Again, the largest changes can be observed in the N-oxide bond length, which shortens by about 0.03 and 0.04 Å. Basically, a trend of slightly elongated bond lengths within the tetrazolate ring and also the azo group is observed. Exact values are listed in the Supporting Information, Table S4. In the structure of compound **5**, layers that run parallel to the b axes are formed (Figure 6 B). These layers are formed by the hexa-fold coordination mode of the potassium cations to two oxygen and four nitrogen atoms shown in Figure 6 C.

Hydroxylammonium 5,5′-azo-bis(1-oxidotetrazolate) (**6**) and ammonium 5,5′-azo-bis(1-oxidotetrazolate) (**7**), as shown in Figure 7 and Figure 8, respectively, both crystallize in the space group $P2_1/c$ with two cation/anion pairs in the unit cell. Interestingly, compound **6** crystallizes with a lower density (1.778 g cm^{-3}) than compound **7** (1.800 g cm^{-3}), which is quite uncommon.[43] In both structures, the N2 ni-

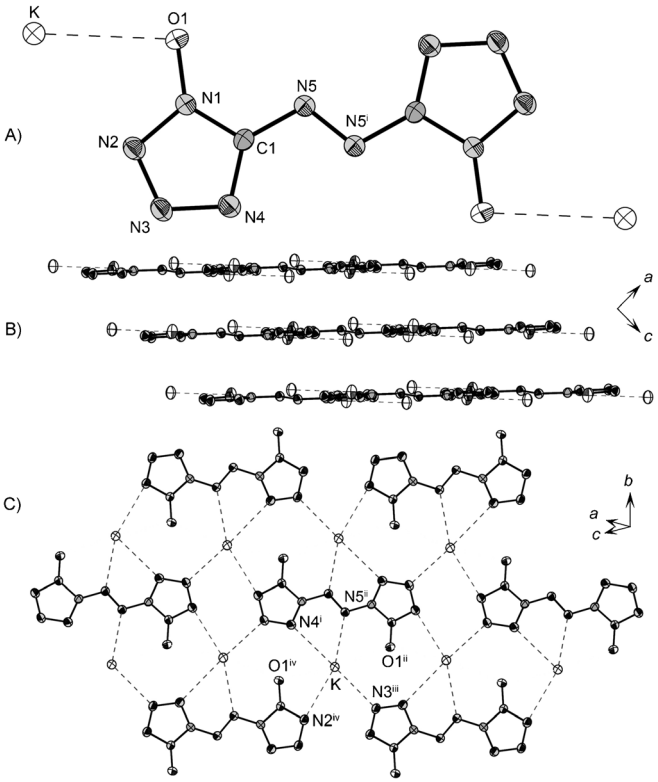


Figure 6. A) Molecular unit of compound **5**; ellipsoids are set at 50% probability. B) View through the layer structures along the *b* axis. C) View of one layer in the structure of compound **5**. Selected coordination distances [Å]: K–N4^{i}: 3.101(3), K–N5^{ii}: 2.950(3), K–O1^{ii}: 2.968(2), K–N3^{iii}: 2.897(3), K–N2^{iv}: 3.045(3), K–O1^{iv}: 2.849(2). Symmetry codes i) $1-x$, $-y$, $2-z$; ii) x, $0.5-y$, $-0.5+z$; iii) $-x$, $-y$, $1-z$; iv) $1+x$, y, z.

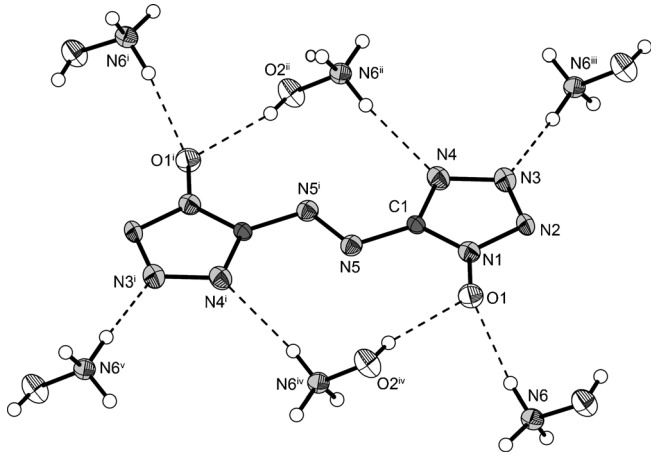


Figure 7. Image of the hydrogen bonds of one 5,5′-azo-bis(1-oxidotetrazolate) dianion in the structure of compound **6**. Symmetry codes: i) $1-x$, $1-y$, $-z$; ii) $1-x$, $0.5+y$, $0.5-z$; iii) $1+x$, $0.5-y$, $0.5+z$; iv) x, $0.5-y$, $-0.5+z$; v) $-x$, $0.5-y$, $-0.5-z$.

trogen atoms do not participate in any hydrogen bonds. The structure of the hydroxylammonium cation, with a N–O bond length of 1.414(3) Å, is similar to literature values.[42]

Crystalline hydrazinium 5,5′-azo-bis(1-oxidotetrazolate) exists in (at least) two polymorphs, both of which crystallize in the monoclinic space group $P2_1/c$ and are obtained simultaneously from water. The molecular moieties of low-density polymorph **8a** (1.673 g cm^{-3}) and high-density polymorph **8b** (1.725 g cm^{-3}) are shown in Figure 9. In the case of compound **8a**, the protonated hydrazinium nitrogen atom N6 is coordinated to the N-oxide oxygen atom, whereas, in compound **8b**, the situation is reversed. The bond lengths and angles, including those of the hydrazinium cations, are very similar.

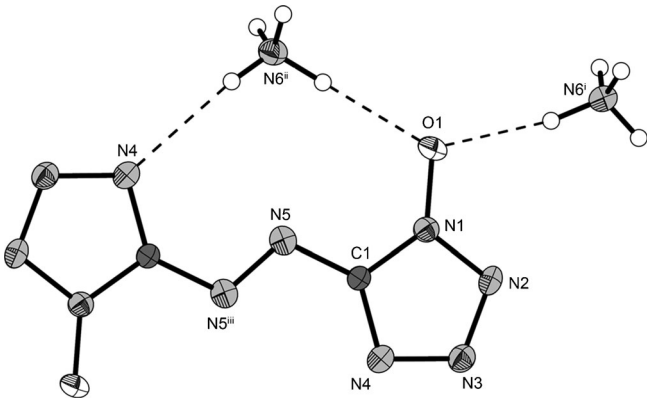


Figure 8. Molecular unit of compound **7**, which shows the labeling scheme; ellipsoids are set at 50% probability. Symmetry codes: i) $1+x$, y, z; ii) $1-x$, $0.5+y$, $0.5-z$; iii) $1-x$, $1-y$, $-z$.

Bis(1-hydroxytetrazolyl)hydrazine (**9**) was obtained as its crystalline sesquihydrate (monoclinic, *C*2/*c*) from water. The asymmetric unit consists of two bistetrazole molecules and three water molecules. One bis(1-hydroxytetrazolyl)hydrazine moiety is shown in Figure 10. The density of 1.707 g cm^{-3} is significantly lower than that of its corresponding water-free non-*N*-oxide, bis(tetrazolyl)hydrazine (1.841 g cm^{-3}).[22] In contrast to hydrazine (point group C_2) the bistetrazole molecule has C_1 symmetry in the solid state. Of course, the hydrazine N5–N6 bond length (1.395 Å) is significantly longer than that in the azo derivatives (mean value: 1.27 Å). The average N–O distance of 1.36 Å is the longest observed in this work.

NMR spectroscopy: All of the NMR spectra were performed in [D$_6$]DMSO. In the ^{1}H NMR spectrum of compound **1**, two signals were observed at $\delta = 6.6$ and 12.7 ppm for the amino and hydroxy protons, respectively. The ^{13}C NMR spectrum exhibits one signal at $\delta = 150.5$ ppm, which is shifted upfield compared to that of 5-aminotetrazole ($\delta = 156.6$ ppm). Compound **4** shows a broad signal at $\delta = 10.6$ ppm in the ^{1}H NMR spectrum, as well as a shift to $\delta = 154.3$ ppm in the ^{13}C NMR spectrum, which is also upfield shifted compared to azotetrazolate ($\delta = 173.2$ ppm).[36] The expected shift to higher field can also be observed for compound **9**, which shows a ^{13}C NMR resonance at $\delta =$ 151.1 ppm, compared to $\delta = 159.7$ ppm for the non-oxide derivative. The ^{15}N NMR spectra (with $MeNO_2$ as an external standard) of compounds **1**, **4**, and **9** are summarized in Figure 11; the spectra for compounds **1** and **9** are proton decoupled. The chemical shift of nitrogen atom N1 compared to atom N4 illustrates the electron-donating effect of a lone

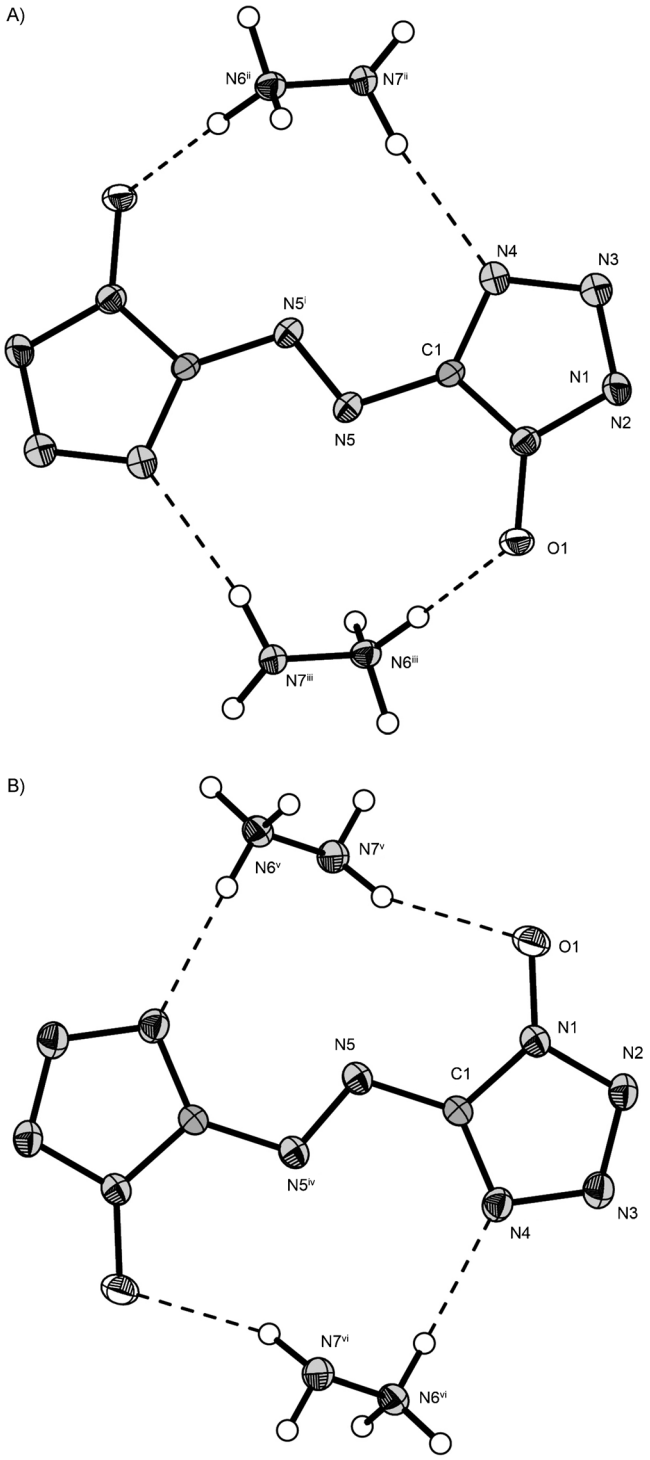


Figure 9. Molecular moieties of polymorphs A) **8a** and B) **8b**. Symmetry codes: i) $-x$, $1-y$, $-z$; ii) $-1+x$, $0.5-y$, $-0.5+z$; iii) $1-x$, $0.5+y$, $0.5-z$; iv) $-x$, $2-y$, $-z$; v) x, $1+y$, z; vi) $-x$, $1-y$, $-z$.

pair of the oxygen atom that is connected to the 1-position of the tetrazole.

Physicochemical properties: Because all of the materials investigated herein are highly energetic compounds, their energetic behaviors were investigated.

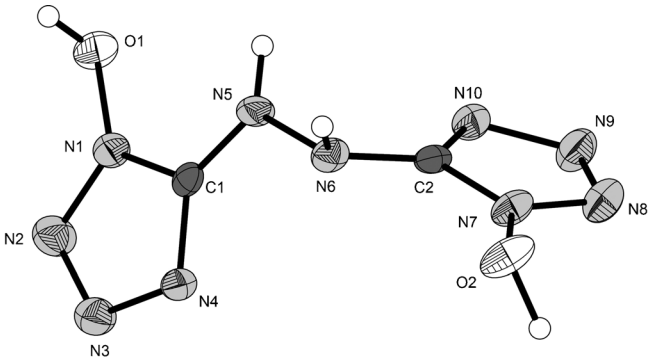


Figure 10. Crystal structure of bis(1-hydroxytetrazolyl)hydrazine (**9**); ellipsoids are set at 50% probability. Crystallized water molecules are omitted.

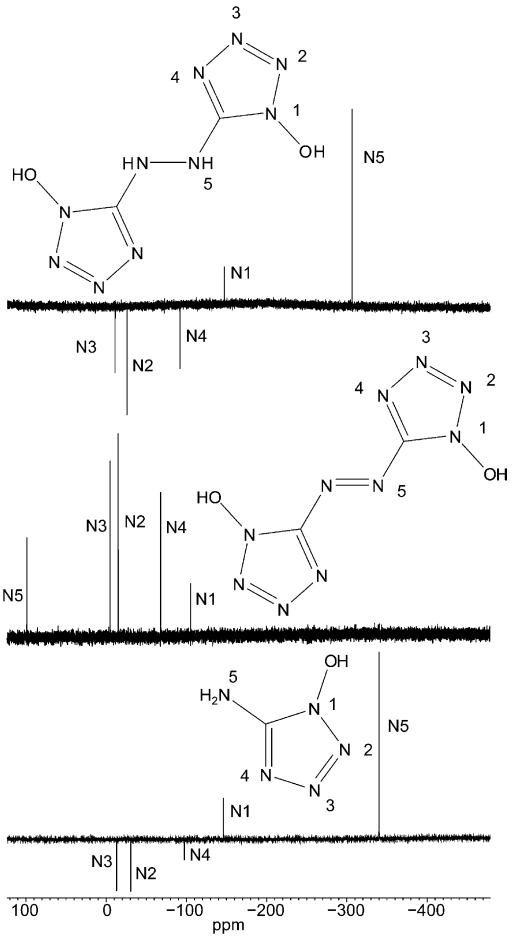


Figure 11. $^{15}N\{^{1}H\}$ NMR spectra of compounds **1** and **9** and ^{15}N NMR spectrum of compound **4** in $[D_6]$DMSO. (**1** 40.5 MHz): $\delta = -12.9$ (N3), -30.6 (N2), -97.4 (N4), -146.2 (N1), -340.0 ppm (N5); (**4** 40.5 MHz): $\delta = 98.6$ (N5), -5.2 (N3), -15.1 (N2), -68.1 (N4), -105.6 ppm (N1); (**9** 40.5 MHz): $\delta = -11.1$ (N3), -25.9 (N2), -91.9 (N4), -147.0 (N1), -306.5 ppm (N5).

Thermal behavior. The thermal behavior of all of the compounds synthesized herein was investigated on a Linseis PT10 DSC with a heating rate of 5 °C min^{-1} by using approximately 1.5 mg of material. All of the DSC curves are sum-

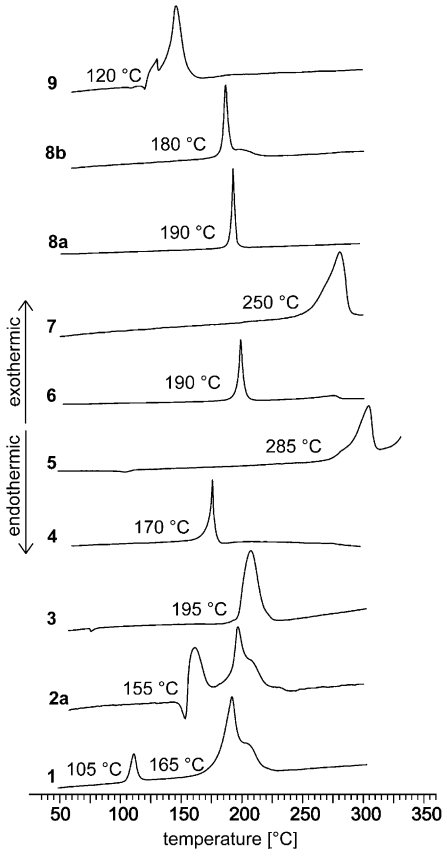


Figure 12. DSC plots of compounds **1**–**9**.

marized in Figure 12. N-oxidation at either the 1- or 2-positions of the tetrazoles leads to a decrease in the thermal stability of the protonated species, at least for 5-nitrotetrazole,[17b,29] 5,5′-bistetrazole,[34] and 5-azidotetrazole.[30] In this case, compounds **1** and **9** decompose at 105 °C and 120 °C, which is quite a bit lower than those of 5-aminotetrazole (199 °C)[16] and bistetrazolylhydrazine (207 °C).[22] Although compound **1** shows two exothermic peaks, the second one at 165 °C is still lower than the decomposition point of 5-aminotetrazole. In the case of compound **4**, there is no reference because 5,5′-azotetrazole is an unstable molecule and, therefore, the effect of the oxide stabilizes the molecule with a decomposition point of 170 °C. The 5,5′-azo-bis(1-oxido-tetrazolate) dianion is even more stable than azotetrazolate. Potassium salt **5** decomposes at 285 °C, whereas potassium azotetrazolate already decomposes at 243 °C.[41] The difference between the decomposition temperatures of the ammonium salts is even larger: Compound **7** decomposes at 250 °C, whereas $(NH_4)_2AzT$[48] already decomposes at 190 °C. The nitrogen-rich salts of compound **4** show decomposition temperatures between 180 °C and 250 °C. The fact that the two polymorphs of compound **8** show different decomposition temperatures of 190 °C (**8a**) and 180 °C (**8b**) is remarkable. With respect to the 1-oxido-5-aminotetrazolate salts, low-density polymorph **2a** starts to melt (with decomposition) at 155 °C, whereas compound **3** decomposes at 195 °C.

Heats of formation, sensitivity, and detonation parameters. For a complete discussion of the methods that were employed, see the Supporting Information. The explosive properties of all of these compounds are listed in Table 1 and Table 2. Compound **1** and its hydroxylammonium salt (**2**) already had high detonation velocities (V_{det}) of 8609 m s^{-1} and 9056 m s^{-1} and were moderately sensitive, with an impact sensitivity of 10 J and friction sensitivities of 108 and 360 N, respectively; the monoclinic form of compound **2b** even has a velocity of detonation of 9312 m s^{-1}, owing to its higher

Table 1. Explosive and detonation parameters of compounds **1**–**4**, RDX, and HMX.

	1	**3**	**2a**	**2b**	**4**	RDX	HMX
formula	CH_3N_5O	CH_6N_6O	$CH_6N_6O_2$	$CH_6N_6O_2$	$C_2H_2N_{10}O_2$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$
M_w [g mol^{-1}]	101.07	118.12	134.12	134.12	198.10	222.12	296.16
IS [J][a]	10	>40	10	–	<1	7.5[45]	7[45]
FS [N][b]	108	>360	>360	–	<5	120[45]	112[45]
ESD [J][c]	0.6	1.5	0.3	–	0.01	0.2	0.2
N [%][d]	69.29	71.16	62.67	62.67	70.70	37.84	37.84
Ω [%][e]	−39.57	−54.19	−35.79	−35.79	−24.23	−21.61	−21.61
$T_{dec.}$ [°C][f]	105	195	155	–	170	205	275
ρ [g cm^{-3}][g]	1.695	1.530	1.664	1.735	1.902	1.858 (90 K)[46]	1.944 (100 K)[47]
$\Delta_f H_m°$ [kJ mol^{-1}][h]	255.7	226.7	284.8	278.3	883.2	86.3	116.1
$\Delta_f U°$ [kJ kg^{-1}][i]	2639.8	2055.7	2252.8	2204.3	4545.3	489.0	492.5
EXPLO5 values (V5.05)							
$-\Delta_{Ex}U°$ [kJ kg^{-1}][j]	5139	4559	6032	5984	6648	6190	6185
T_{det} [K][k]	3628	3007	3771	3725	4973	4232	4185
P_{CJ} [kbar][l]	298	245	327	357	424	380	415
V_{det} [m s^{-1}][m]	8609	8225	9056	9312	9548	8983	9221
V_o [L kg^{-1}][n]	813	888	892	892	733	734	729
I_S [s][o]	237	222	263	262	271	258	258

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance ($\Omega = (x\mathrm{O} - 2y\mathrm{C} - 1/2\,z\mathrm{H})M/1600$). [f] Decomposition temperature (from DSC, $\beta = 5$ °C min^{-1}). [g] From X-ray diffraction analysis. [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products). [o] Specific impulse under isobaric (60 bar) conditions.

Table 2. Explosive and detonation parameters of **5–9** and ammonium azotetrazolate (**$(NH_4)_2AzT$**).

	5	**7**	$(NH_4)_2AzT$[48]	**6**	**8a**	**8b**	**9**
formula	$C_2N_{10}O_2K_2$	$C_2H_8N_{12}O_2$	$C_2H_8N_{12}$	$C_2H_8N_{12}O_4$	$C_2H_{10}N_{14}O_2$	$C_2H_{10}N_{14}O_2$	$C_2H_7N_{10}O_{3.5}$
M_w [g mol^{-1}]	274.28	232.16	200.17	264.16	262.19	262.19	227.16
IS [J][a]	20	3	6	15	3		1
FS [N][b]	>360	160	44	54	20		<5
ESD [J][c]	0.35	0.2	0.18	0.2	0.7		0.007
N [%][d]	51.07	72.40	83.97	63.63	74.79	74.79	61.66
Ω [%][e]	−17.5	−41.34	−63.94	−24.22	−42.71	−42.71	−28.17
$T_{dec.}$ [°C][f]	285	250	190	190	190	180	120
ρ [g cm^{-3}][g]	2.200	1.800	1.562	1.778	1.673	1.725	1.707
$\Delta_f H_m°$ [kJ mol^{-1}][h]	240.2	551.7	551.4	730.9	932.5	916.7	390.1
$\Delta_f U°$ [kJ kg^{-1}][i]	930.3	2493.1	2878.0	2878.7	3678.5	3618.1	1829.3
EXPLO5 values (V5.05)							
$-\Delta_{Ex}U°$ [kJ kg^{-1}][j]	–	4793	3437	6456	5817	5756	5478
T_{det} [K][k]	–	3313	2565	4310	3748	3711	3851
P_{CJ} [kbar][l]	410[p]	338	216	375	329	350	312
V_{det} [m s^{-1}][m]	9753[p]	9032	7788	9348	9066	9246	8711
V_o [L kg^{-1}][n]	–	837	823	841	857	856	833
I_S [s][o]		231	207	270	258	257	249

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance ($\Omega=(x\mathrm{O}-2y\mathrm{C}-1/2\,z\mathrm{H})M/1600$). [f] Decomposition temperature (from DSC, $\beta=5$ °C min^{-1}). [g] From X-ray diffraction analysis. [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products). [o] Specific impulse under isobaric (60 bar) conditions. [p] Calculated by Dr. Betsy Rice (ARL) with Cheetah 6.

density. Compound **4** impresses with its tremendously high heat of formation (883 kJ mol^{-1}). In combination with a high density of 1.902 g cm^{-3}, the compound performs very well, with a detonation velocity of 9548 m s^{-1} and a detonation pressure (p_{CJ}) of 424 kbar, whilst being very sensitive towards friction and impact. The specific impulse of 271 s is remarkably high. This compound has the properties of a primary explosive, thereby showing almost (!) detonative combustion (see the video in the Supporting Information). The heat of formation of compound **7** is quite similar to that of $(NH_4)_2AzT$[48], whereas its density (1.800 g cm^{-3}) is higher than that of the non-oxide derivative. In combination with its better oxygen balance, compound **7** shows quite high performance (9032 m s^{-1} and 338 kbar) compared to only 7788 m s^{-1} and 216 kbar for the tetrazole, thus confirming the comparatively favorable properties of a tetrazole oxide. The impact sensitivities of both compounds are similar, whereas the effects of an oxide lead to a significant decrease in friction sensitivity. This effect in more-strongly manifested for the potassium salt. Whilst anhydrous K_2AzT is a quite sensitive compound, detonating in a flame, compound **5** possesses impact and friction sensitivities of 20 J and >360 N, respectively. Once ignited, compound **5** calmly deflagrates, thereby further underlining the favorable properties of a tetrazoleoxide. Owing to its high density of 2.20 g cm^{-3}, compound **5** shows quite high calculated performance values of $V_{det}=9753$ m s^{-1} and $p_{CJ}=410$ kbar (calculated with Cheetah 6). In general, all of the high-nitrogen-content salts of compound **4**, as well as the compound itself, perform quite well, with velocities of detonation in the range 9032–9548 m s^{-1} and detonation pressures in the range 329–424 kbar. Compounds **4**, **6**, and **7** were tested for their combustion behavior; they combusted smokelessly, with the formation of almost no solid residues, as shown in the videos in the Supporting Information. Similar to compound **4**, anhydrous **9** is a quite-sensitive solid. Thus, the performance data for compound **9** are indicated for its sesquihydrate.

Conclusion

For the first time, 1-hydroxy-5-aminotetrazole (**1**) was synthesized by the reaction of cyanogen azide and hydroxylamine and was azo-coupled by using potassium permanganate. The resulting 1,1′-dihydroxy-5,5′-azotetrazole (**4**) was reduced with magnesium into 1,2-bis(1-hydroxytetrazolyl)-hydrazine. Compound **1** was converted into its hydroxylammonium (**2**) and ammonium salts (**3**), whilst compound **4** was converted into its potassium (**5**), ammonium (**7**), hydroxylammonium (**6**) and hydrazinium salts (**8**). All of these compounds were characterized by low-temperature X-ray diffraction. Polymorphs of compounds **2** and **8** were detected and explored. In addition, all of these compounds were analyzed by multinuclear NMR, IR, and Raman spectroscopy, differential scanning calorimetry, and their sensitivities were determined according to BAM standards. Their energetic properties, such as heat of formation and detonation parameters, were calculated. These compounds are high-performing explosives, with six compounds showing a velocity of detonation over 9000 m s^{-1}. Because azotetrazole dioxide and its salts are more-easily prepared and are chemically and thermally more stable than azotetrazole and azotetrazolate, compounds **6–8** could be used as explosive or propellant ingredients without the disadvantages of the azotetrazolate anion.

Experimental Section

General procedures: Raman spectra were recorded on a Bruker Multi-RAM FT-Raman instrument that was fitted with a liquid-nitrogen-cooled germanium detector and a Nd:YAG laser ($\lambda = 1064$ nm). IR spectra were recorded on a Perkin–Elmer Spectrum BX-FTIR spectrometer that was equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature on solid samples. NMR spectra were recorded at 25 °C on a JEOL Eclipse 400 ECX instrument; chemical shifts were determined with respect to external $SiMe_4$ (^1H: 400.2 MHz, ^{13}C: 100.6 MHz) or $MeNO_2$ (^{14}N: 29.0 MHz). Elemental analysis was performed on an Elementar Vario EL analyzer. Decomposition points were determined by differential scanning calorimetry (DSC) on a Linseis DSC-PT10 at a heating rate of 5 °C min^{-1}. Sensitivity data (impact, friction, and electrostatic discharge) were recorded by using a drophammer, a friction tester, and an electrostatic discharge device that was analogous to BAM (Bundesanstalt für Materialforschung und prüfung).[49]

XRD was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage: 50 kV, current: 40 mA) and a KappaCCD detector by using Mo Kα radiation ($\lambda = 0.71073$ Å) at low temperature (173 K). Data-collection and -reduction were performed by using the CRYSALISPRO software.[50] The structures were solved with either SHELXS-97[51] or with SIR-92,[52] refined with SHELXL-97,[53] and, finally, checked by using the PLATON[54] software that was integrated into the WINGX[55] software suite. All hydrogen atoms were found and freely refined. Friedel pairs of non-centrosymmetric space groups were merged by using the MERG3 command. The absorptions were corrected by using a Scale3 Abspack multi-scan method.[56]

CCDC-897251 (**1**), CCDC-897256 (**2a**), CCDC-897257 (**2b**), CCDC-897252 (**3**), CCDC-897254 (**4**), CCDC-897253 (**5**), CCDC-897255 (**6**), CCDC-897258 (**7**), CCDC-897259 (**8a**), CCDC-897260 (**8b**) and CCDC-897941 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution! All of these investigated compounds are potentially explosive energetic materials. Although no hazards were observed during the preparation and handling of these compounds, nevertheless, this property necessitates taking additional meticulous safety precautions (earthed equipment, Kevlar gloves, Kevlar sleeves, face shield, leather coat, and ear plugs).

Hydroxylammonium aminotetrazole-1-oxide (2a): Cyanogen bromide (2.12 g, 20 mmol) was dissolved in MeCN (100 mL). The solution was cooled at 0–5 °C and sodium azide (1.40 g, 21.5 mmol) was added. After stirring for 4 h in an ice bath, the suspension was filtered and washed with MeCN (10 mL). Caution! Never let the filter paper dry out! The solution was cooled to −20 °C and a 50 % solution of hydroxylamine (2.64 g) in MeCN (20 mL) was added in one portion. The resulting suspension was stirred for 60 min at RT and then filtered. The solid was washed with Et_2O (30 mL) and dried in air to afford compound **2a** (1.29 g, 48 % yield). After standing for a further 3 h at RT, pure compound **2a** (0.58 g, 22 % yield) was isolated from the filtrate.

^1H NMR ([D$_6$]DMSO, 25 °C): $\delta = 8.46$, 8.22 ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = 149.3$ ppm; IR (ATR): $\tilde{\nu} = 2464$ (m), 1739 (w), 1644 (w), 1557 (m), 1531 (m), 1479 (w), 1308 (m), 1269 (w), 1257 (w), 1204 (w), 1164 (w), 1144 (w), 1127 (w), 1102 (m), 1002 (m), 830 (s), 801 (w), 781 (vs), 721 (m), 668 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 3122$ (27), 1637 (21), 1594 (28), 1479 (39), 1264 (62), 1203 (11), 1121 (18), 1102 (28), 1000 (100), 796 cm^{-1} (91); DSC (5 °C min^{-1}): 155 °C (dec.); elemental analysis calcd [%] for $CH_6N_6O_2$ (134.1): C 8.96, H 4.51, N 62.67; found: C 9.46, H 4.33, N 62.39; BAM drophammer: 10 J; friction tester: 360 N; ESD: 0.3 J.

Hydroxyaminotetrazole (1): Crude compound **2** was dissolved in 2 M HCl and pure HAT was crystallized, filtered, and dried.

^1H NMR ([D$_6$]DMSO, 25 °C): $\delta = 12.81$, 6.66 ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = 150.5$ ppm; $^{15}N\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = -12.9$ (N3), −30.6 (N2), −97.4 (N4), −146.2 (N1), −340.0 ppm (N5); IR (ATR): $\tilde{\nu} = 3423$ (w), 3165 (m), 2672 (m), 2588 (m), 1640 (vs), 1522 (m), 1467 (w), 1447 (w), 1419 (m), 1333 (w), 1298 (s), 1262 (s), 1173 (w), 1120 (w), 1065 (m), 1004 (w), 913 (m), 810 (m), 723 (m), 687 (m), 629 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 3324$ (13), 1662 (14), 1472 (7), 1450 (4), 1336 (34), 1320 (10), 1282 (15), 1177 (7), 1126 (6), 1070 (16), 796 (100), 712 cm^{-1} (15); DSC (5 °C min^{-1}): 105 °C (dec.); elemental analysis calcd [%] for CH_3N_5O (101.07): C 11.88, H 2.99, N 69.29; found: C 12.32, H 2.92, N 68.54; BAM drophammer: 10 J; friction tester: 108 N; ESD: 0.6 J.

Ammonium aminotetrazole-1-oxide (3): Compound **1** (1.01 g, 10 mmol) was dissolved in water (30 mL) and 2 M NH_3 (6 mL) was added. The solvent was evaporated and the product was obtained (1.12 g, 95 % yield) as a white crystalline solid.

^1H NMR ([D$_6$]DMSO, 25 °C): $\delta = 6.72$, 5.32 ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = 148.0$ ppm; IR (ATR): $\tilde{\nu} = 3189$ (s), 2727 (s), 2152 (w), 1930 (w), 1635 (vs), 1577 (s), 1477 (s), 1454 (s), 1387 (m), 1297 (s), 1256 (s), 1164 (w), 1135 (w), 1099 (m), 1000 (w), 789 (w), 711 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 3165$ (30), 1639 (12), 1595 (25), 1479 (29), 1395 (8), 1258 (91), 1160 (7), 1133 (10), 1103 (26), 1000 (23), 802 (100), 706 cm^{-1} (4); DSC (5 °C min^{-1}): 195 °C (dec.); elemental analysis calcd [%] for CH_6N_6O (118.1): C 10.17, H 5.12, N 71.16; found: C 10.77, H 5.25, N 69.14; BAM drophammer: > 40 J; friction tester: > 360 N; ESD: > 1.5 J.

Azotetrazole-1,1′-dioxide dipotassium salt (5): Crude compound **2** (2.165 g, 16.1 mmol) was dissolved in water (50 mL) and 2 M KOH (11 mL) was added. Then, the solution was heated to 70 °C and a solution of $KMnO_4$ (2.543 g, 16 mmol) in hot water was added dropwise. After a total stirring time of 30 min at 70 °C, MeOH (10 mL) was added and the mixture was stirred for a further 10 min at 70 °C. The suspension was filtered hot through celite and the filtrate was concentrated until the red product started to precipitate. The solution was then left to crystallize at RT. The precipitation was completed by the addition of EtOH. The precipitate was filtered and washed with EtOH and Et_2O to afford pure compound **5** (1.726 g, 78 % yield) as an orange-red solid.

IR (ATR): $\tilde{\nu} = 1738$ (w), 1471 (w), 1428 (m), 1378 (w), 1271 (m), 1216 (m), 1143 (m), 1066 (w), 1003 (w), 784 (vs), 740 (w), 717 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 1388$ (100), 1205 (9), 1157 (5), 1085 (8), 1018 (3), 922 cm^{-1} (15); DSC (5 °C min^{-1}): 285 °C (dec.); elemental analysis calcd [%] for $K_2C_2N_{10}O_2$ (274.28): C 8.76, N 51.07; found: C 9.21, N 50.96; BAM drophammer: 20 J; friction tester: 360 N; ESD: 0.35 J.

1,1′-Dihydroxyazotetrazole (4): Compound **5** (2.74 g, 10 mmol) was dissolved in 2 M HCl (50 mL) and the solution was extracted with EtOAc (30 mL portions) until the color of the aqueous phase became only slightly yellow. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo to afford the free acid (1.80 g, 91 % yield) as an orange solid.

^1H NMR ([D$_6$]DMSO, 25 °C): $\delta = 10.62$ ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = 154.3$ ppm; ^{15}N NMR ([D$_6$]DMSO, 25 °C): $\delta = 98.6$ (N5), −5.2 (N3), −15.1 (N2), −68.1 (N4), −105.6 ppm (N1); IR (ATR): $\tilde{\nu} = 2196$ (m), 1529 (m), 1402 (m), 1240 (s), 1162 (m), 1077 (s), 867 (vs), 770 (s), 738 (s), 725 (s), 708 (s), 681 cm^{-1} (s); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 1628$ (4), 1423 (100), 1224 (52), 1163 (7), 1115 (34), 1036 (3), 925 (22), 724 (2), 549 cm^{-1} (9); DSC (5 °C min^{-1}): 170 °C (dec.); BAM drophammer: < 1 J; friction tester: < 5 N; ESD: 0.01 J.

Azotetrazole-1,1′-dioxide dihydroxylammonium salt (6): Compound **5** (2.74 g, 10 mmol) was dissolved in 2 M HCl (50 mL) and the solution was extracted with EtOAc (30 mL portions) until the color of the aqueous phase was only slightly yellow. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. The solid was dissolved in MeOH (20 mL) and a 50 % solution of hydroxylamine (1.32 g) in MeOH (10 mL) was added to the solution. The suspension was diluted with Et_2O (10 mL) and the orange solid was filtered and dried to give pure compound **6** (2.51 g, 95 % yield).

^1H NMR ([D$_6$]DMSO, 25 °C): $\delta = 10.33$ ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta = 153.6$ ppm; IR (ATR): $\tilde{\nu} = 2922$ (w), 2695 (m), 1739 (w), 1605 (w), 1510 (w), 1481 (m), 1432 (m), 1285 (w), 1268 (vs), 1226 (s), 1148 (w), 1096 (w), 1010 (m), 793 (s), 738 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu} = 1389$ (100), 1218 (10), 1172 (7), 1157 (5), 1111 (6), 1026 (4),

939 (4), 923 (5), 736 cm^{-1} (2); DSC (5 °C min^{-1}): 190 °C (dec.); elemental analysis calcd [%] for $C_2H_8N_{12}O_4$ (264.16): C 9.09, H 3.05, N 63.63; found: C 9.75, H 2.85, N 63.90; BAM drophammer: 15 J; friction tester: 54 N; ESD: 0.2 J.

Azotetrazole-1,1′-dioxide diammonium salt (7): Compound **5** (2.74 g, 10 mmol) was dissolved in 2 M HCl (50 mL) and the solution was extracted with EtOAc (30 mL portions) until the color of the aqueous phase was only slightly yellow. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. The solid was dissolved in EtOH (20 mL) and gaseous ammonia was bubbled through the solution. The suspension was diluted with Et_2O (10 mL) and the orange solid was filtered and dried to give pure compound **7** (2.06 g, 89 % yield).

^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.38 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 153.8 ppm; IR (ATR): $\tilde{\nu}$ = 3195 (w), 3029 (m), 2836 (w), 1471 (w), 1419 (s), 1263 (vs), 1222 (m), 1147 (w), 1068 (w), 1004 (w), 782 (s), 738 (w), 721 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 1382 (100), 1204 (12), 1157 (6), 1088 (8), 1015 (5), 922 cm^{-1} (16); DSC (5 °C min^{-1}): 250 °C (dec.); elemental analysis calcd [%] for $C_2H_8N_{12}O_2$ (232.16): C 10.35, H 3.47, N 72.40; found: C 11.00, H 3.23, N 72.57; BAM drophammer: 3 J; friction tester: 160 N; ESD: 0.2 J.

Azotetrazole-1,1′-dioxide dihydrazinium salt (8): Compound **5** (10 mmol) was dissolved in 2 M HCl (50 mL) and the solution was extracted with EtOAc (25 mL portions) until the color of the aqueous phase was only slightly yellow. The organic phase was dried over magnesium sulfate and evaporated to give azotetrazole dioxide as an orange solid. The acid was dissolved in MeOH (10 mL) and hydrazine hydrate (20 mmol) was added. The precipitate was filtered and dried to give an orange solid that consisted of a mixture of compounds **8a** and **8b**.

^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.27 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 153.9 ppm; IR (ATR): $\tilde{\nu}$ = 3311 (w), 3240 (w), 2919 (w), 2797 (w), 2655 (w), 2144 (w), 1657 (w), 1639 (w), 1614 (w), 1598 (w), 1547 (m), 1474 (m), 1455 (w), 1419 (m), 1411 (m), 1266 (s), 1216 (m), 1154 (m), 1145 (s), 1114 (s), 1075 (m), 1014 (w), 970 (s), 782 (vs), 740 (m), 725 (m), 699 cm^{-1} (w). Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1386 (100), 1203 (10), 1156 (3), 1085 (6), 1026 (2), 921 (9), 121 cm^{-1} (2); DSC (5 °C min^{-1}):187 °C (dec.); elemental analysis calcd [%] for $C_2H_{10}N_{14}O_2$ (262.19): C 9.16, H 3.84, N 74.79; found: C 9.79, H 3.84, N 73.77; BAM drophammer: 3 J; friction tester: 20 N; ESD: 0.7 J.

Bistetrazolylhydrazinedioxide (9): K_2AzTO (10 mmol) was dissolved in hot water (50 mL) and powdered magnesium (3 g) was added. The solution was boiled until the color disappeared after a few minutes. Then, the solution was rapidly cooled over ice, filtered, and acidified with concentrated hydrochloric acid to pH 1. The solution was extracted five times with EtOAc (20 mL) and the organic phase was dried over magnesium sulfate and evaporated. The residue was crystallized from water, thereby yielding complex **9**·1.5 H_2O (1.59 g, 70 % yield) as colorless crystals.

^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.38 ppm; ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 13.37, 9.49 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 151.1 ppm; ^{15}N{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = −11.1 (N3), −25.9 (N2), −91.9 (N4), −147.0 (N1), −306.5 ppm (N5); IR (ATR): $\tilde{\nu}$ = 3307 (w), 2896 (w), 1621 (s), 1539(m), 1514 (m), 1466 (w), 1435 (w), 1353 (w), 1312 (w), 1245 (vs), 1212 (w), 1157 (w), 1143 (m), 1115 (w), 1090 (m), 1036 (w), 1004 (w), 973 (w), 862 (m), 789 (w), 716 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3305 (14), 3110 (15), 1630 (17), 1545 (5), 1523 (4), 1389 (100), 1319 (16), 1268 (17), 1214 (10), 1145 (13), 1098 (10), 1006 (9), 980 (5), 929 (10), 840 (14), 689 (6), 532 cm^{-1} (4); DSC (5 °C min^{-1}): 120 °C (dec.).

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Oxalylhydrazinium Nitrate and Dinitrate—Efficiency Meets Performance

DENNIS FISCHER,[1] THOMAS M. KLAPÖTKE,[1,2] AND JÖRG STIERSTORFER[1]

[1]Department of Chemistry, Ludwig-Maximilian University Munich, Energetic Materials Research, Germany
[2]Department of Mechanical Engineering, Center for Energetic Concepts Development, University of Maryland, College Park, Maryland

Oxalylhydrazinium nitrate (OHN) and dinitrate (OHDN) were synthesized by protonation of oxalyldihydrazide with nitric acid. The synthesis is extremely cost effective (~$40/kg at the lab scale) and can be carried out in large scales and very good yields. OHN and OHDN were intensively characterized by low-temperature X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and vibrational spectroscopy. These new organic nitrate salts could be used as powerful ingredients in energetic formulations due to their low sensitivities (measured by Bundesanstalt für Materialforschung und Pröfung methods). Their thermal stability was investigated by differential scanning calorimetry (DSC) measurements. Further thermal studies of OHN showed compatibility with TNT (2,4,6-trinitrotoluene), DNAN (2,4-dinitroanisole), and RDX (1,3,5-trinitro-1,3,5-triazinane). The theoretical detonation and propulsion parameters of OHN and OHDN were calculated with the EXPLO5.5 code and compared to well-known insensitive explosives. The aquatic toxicity of OHN was determined by the luminescent bacteria inhibition test, yielding a much lower toxicity than RDX.

Keywords compatibility; crystal structure; explosives; nitrates; sensitivity

Introduction

In the last decade, efforts to improve munitions safety and survivability led to the concept of *insensitive munitions*. These munitions must withstand accidents, fires, or enemy attack. Therefore, there is a great demand for new insensitive explosives that also meet military performance criteria. Many examples of low-sensitivity secondary explosives have been described in the literature [1]. Prominent examples of pure compounds are TATB (1,3,5-triamino-2,4,6-trinitrobenzene) [2], ANTA (3-amino-5-nitrotriazole) [3], DINGU (dinitroglycoluryl) [4], TNGU (tetranitroglycoluryl) [5], DNI (2,4-dinitroimidazole) [6], FOX-7 (1,1-dinitro-2,2-diaminoethene) [7], FOX-12 (guanylurea dinitramide) [8], NTO (nitro-triazolone) [9], and LLM-105 (3,5-dinitro-2,6-pyrazinediamine 1-oxide) [10]. Another explosive of interest is DAAF (diaminoazoxyfurazan), which has been intensively investigated by many research groups [11]. However, most of the compounds have lower

Address correspondence to Thomas M. Klapötke, Ludwig-Maximilian University Munich, Energetic Materials Research, Department of Chemistry, Butenandtstr. 5-13, D-81377, Germany. E-mail: tmk@cup.uni-muenchen.de

performances than RDX (1,3,5-trinitro-1,3,5-triazinane, hexogen) and high melting explosive (HMX; octogen) or show extensive preparative routes.

In this article, we present the new weakly sensitive compounds oxalylhydrazinium nitrate (OHN, **2**) and oxalylhydrazinium dinitrate (OHN, **3**) which are characterized by good oxygen balances, promising calculated detonation performance, and an astonishingly facile and low-cost synthesis.

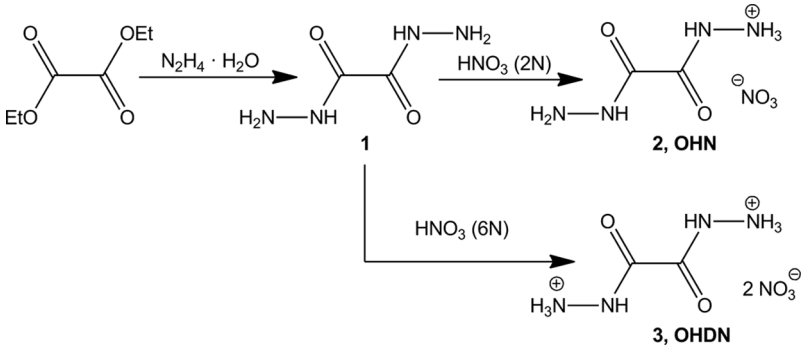
Results and Discussion

The precursor of OHN and OHDN is oxalyldihydrazide (**1**), which was synthesized from diethyl oxalate and hydrazine hydrate [12] by simple dropwise addition of diethyl oxalate to an ethanolic solution of hydrazine hydrate. The product precipitates instantly and therefore the reaction takes only a few minutes, yielding **1** in high purity and almost 100% yield. The nitrate salt **2** can be prepared by dissolving **1** in a slight excess of hot 0.5 M HNO_3. **2** Precipitates almost quantitatively by the addition of cold ethanol and can be collected easily by filtration. The dinitrate salt **3** was prepared in 100% yield similar to **2** but using an excess of 30% hot nitric acid. The synthesis of **2** and **3** is figured in Scheme 1.

In summary, the overall synthesis of **2** and **3** is fast, facile, cost-efficient, and almost quantitative. For the lab scale (up to 1 kg), we estimate the total cost of commercially purchased chemicals and solvents needed for the synthesis of 1 kg OHN to be less than €30 ($40). Considering that lab chemicals are always more expensive than chemicals used at an industrial scale, the material costs for OHN on a large scale are much lower, for example, than the costs for RDX.

Compounds **1**–**3** can be easily identified by nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H-NMR spectrum of **1** shows two singlets at 9.93 and 4.47 ppm for the NH and NH_2 protons, respectively. A signal at 158.4 ppm can be observed in the ^{13}C-NMR spectrum, which is shifted to 157.7 and 157.3 ppm when the compound is protonated with HNO_3 once or twice, respectively. In the ^{1}H-NMR, **2** shows only one broad singlet at 8.28 ppm and **3** shows a broad singlet at 10.58 ppm.

Crystals of **2** and **3** suitable for X-ray analysis (see Experimental section) were obtained from water and dilute nitric acid, respectively. Both salts crystallize in monoclinic space groups (**2**: $C2/c$, **3**: $P2_1/c$). The most important crystallographic data are listed in Table 1. The molecular units are shown in Figs. 1 and 2. The



Scheme 1. Synthesis of oxalyldihydrazide and its nitrate salts **2** and **3**.

Table 1 X-ray data and parameters

Compound	**2**	**3**
Formula	$C_2H_7N_4O_5$	$C_2H_8N_6O_8$
Form. weight (g mol^{-1})	181.13	244.14
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Color/habit	Colorless block	Colorless block
Size (mm)	$0.11 \times 0.15 \times 0.20$	$0.13 \times 0.22 \times 0.30$
a (Å)	10.2076(12)	5.7999(2)
b (Å)	11.0956(9)	7.9900(3)
c (Å)	6.3591(8)	9.0753(3)
α (°)	90	90
β (°)	114.793(14)	97.585(4)
γ (°)	90	90
V (Å^3)	653.84(14)	416.88(3)
Z	4	2
$\rho_{calc.}$ (g cm^{-3})	1.840	1.945
μ (mm^{-1})	0.176	0.195
F(000)	376	252
Theta min–max (°)	4.4, 27.0	4.5, 27.0
Data set	−12:11; −9:14; −8:8	−7:7; −10:10; −11:11
Reflections collected	1,796	4,331
Independent reflections	712	913
R_{int}	0.029	0.027
Observed reflections	512	827
No. parameters	72	90
R_1 (obs)	0.0320	0.0269
wR_2 (all data)	0.0793	0.0739
S	0.92	1.08
Resd. Dens. (e Å^{-3})	−0.28, 0.18	−0.27, 0.40
Solution	SIR-92	SIR-92
Refinement	SHELXL-97	SHELXL-97
Absorption correction	Multiscan	Multiscan
CCDC	864719	902480

formation of intense networks of hydrogen bonds (Fig. 3) yields high (**2**: 1.840 g cm^{-3}) to very high densities (**3**: 1.945 g cm^{-3}). Due to the center of inversion in the cation of **2**, one position of the hydrazinium protons is half-occupied. Therefore, the planar structure of the non-hydrogen atoms within the cations is not affected by the second protonation. The N1–N2 bonds are slightly shorter than N–N single bonds. Further information regarding the crystal structure determination has been deposited as a Crystallographic Information File with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 864719 and 902480.

DSC thermographs of **2**, **3** and their precursor **1** are shown in Fig. 4. All temperatures are given as onset temperature using heating rates of 5° min^{-1}. **1** Melts at 236°C and decomposes subsequently at 245°C, whereas **2** shows a sharp decomposition peak at 273°C. **2** Shows an endothermic signal at 180°C. This could be caused

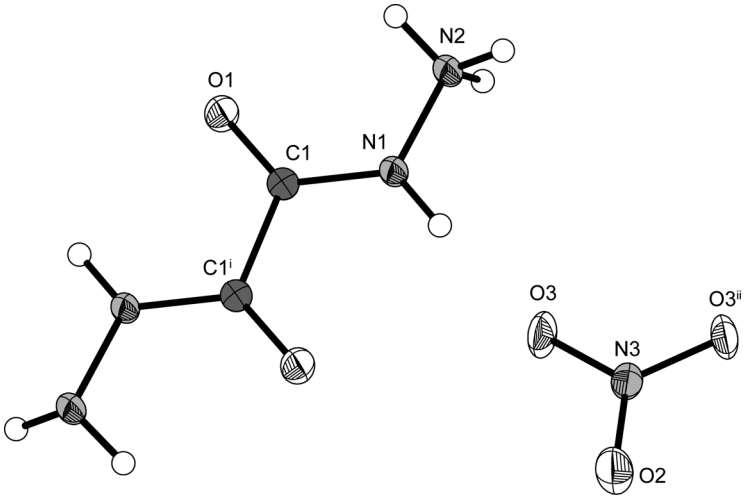


Figure 1. Molecular moiety of oxalylhydrazinium nitrate (**2**). Ellipsoids are drawn at the 50% probability level. (i) $-x$, $-y$, $1-z$; (ii) $1-x$, y, $0.5-z$. Selected bond lengths (Å): O1–C1 1.2278(17), N1–C1 1.3219(19), N1–N2 1.4128(18), O2–N3 1.229(2), O3–N3 1.2534(14), C1–C1^{i} 1.532(2); selected bond angles (°): C1–N1–N2 118.37(13), O1–C1–N1 125.11(13), O1–C1–C1^{i} 122.41(16), N1–C1–C1^{i} 112.45(15), O2–N3–O3 119.79(9), O2–N3–O3 119.79(9), O3–N3–O3^{ii} 120.41(18).

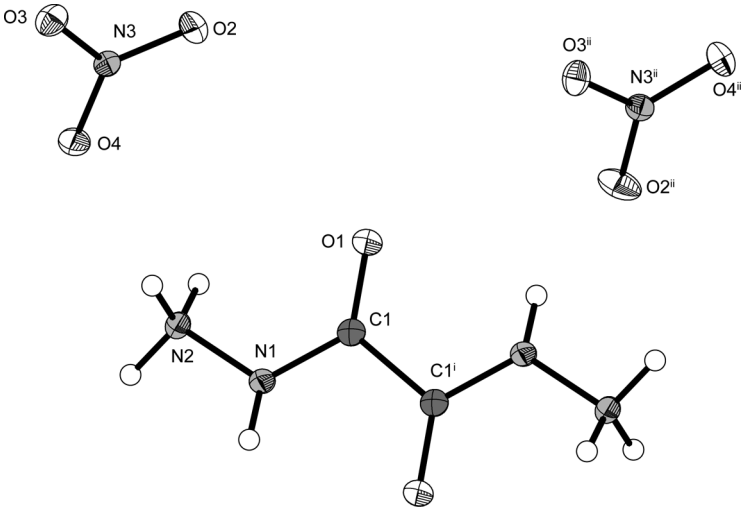


Figure 2. Molecular moiety of oxalylhydrazinium dinitrate (**3**). Ellipsoids are drawn at the 50% probability level. (i) $2-x$, $-y$, $-z$; (ii) $1-x$, $-0.5+y$, $-0.5-z$. Selected bond lengths (Å): O1–C1 1.2273(14), N1–C1 1.3306(15), N1–N2 1.4162(13), C1–C1^{i} 1.531(2), O2–N3 1.2502(13), O3–N3 1.2739(13), O4–N3 1.2381(12); selected bond angles (°): C1–N1–N2 118.03(9), O1–C1–N1 125.35(11), O1–C1–C1^{i} 122.88(13), N1–C1–C1^{i} 111.77(12), O2–N3–O3, O2–N3–O3 119.83(10), O3–N3–O5 121.05(10), O3–N3–O5 119.12(9); torsion angle (°): N2–N1–C1–O1 – 0.19(17), N2–N1–C1–C1^{i} – 179.95(11).

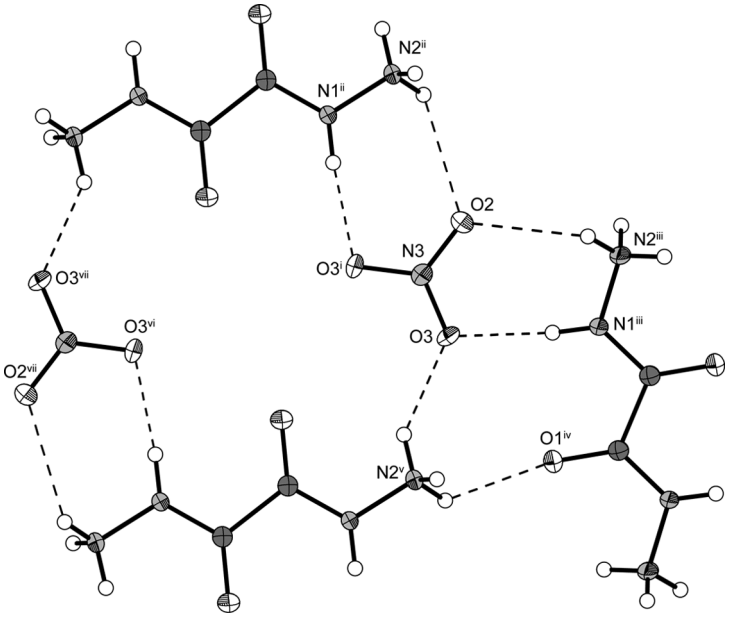


Figure 3. Hydrogen bonding in the structure of **2**. Ellipsoids are drawn at the 50% probability level. Selected hydrogen bonds (D–H $\cdots$ A: d(D–H) (Å), d(H A) (Å), d(D $\cdots$ A) (Å), <(D–H $\cdots$ A) (°)): $N2^{v}$–H2A^{v} O3 0.89(2), 2.125(19), 2.8924(18), 144.3(16); $N2^{v}$–H2B^{v} $O1^{iv}$ 0.90(2), 2.18(2), 2.8087(18), 126.6(16); $N2^{ii}$–H2B $^{ii}\cdots$O2 0.90(2), 2.569(19), 3.0226(18), 112.1(14); $N1^{ii}$–$H1^{ii}$ $O3^{i}$ 0.88(2), 1.95(2), 2.8302(18), 174.6(18); $N1^{iii}$–$H1^{iii}\cdots$O2 0.88(2), 2.629(18), 3.1783(13), 121.3(16); symmetry codes (i) 1 $-x$, y, 0.5 $-z$; (ii) 1 $-x$, $-y$, 1 $-z$; (iii) x, $-y$, -0.5 $+z$; (iv) $-x$, y, 0.5 $-z$; (v) 0.5 $-x$, 0.5 $-y$, 1 $-z$; (vi) 0.5 $+x$, 0.5 $-y$, 0.5 $+z$; (vii) 1.5 $-x$, 0.5 $-y$, 1 $-z$.

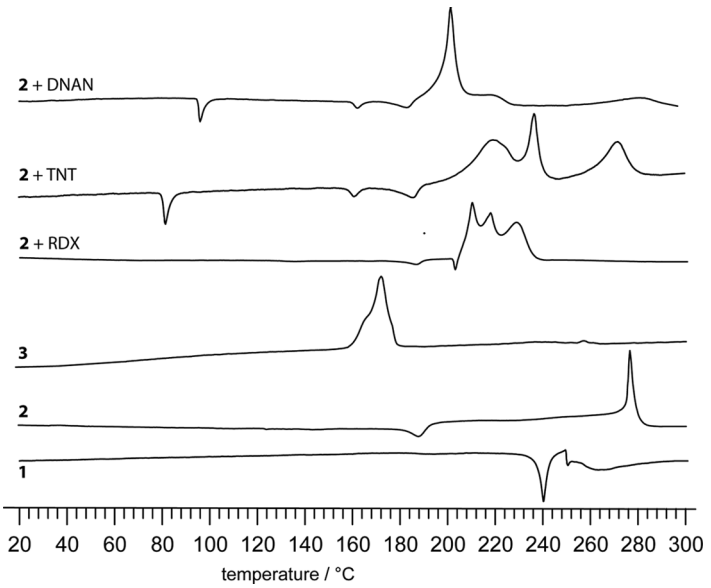


Figure 4. DSC thermographs of **1** and its nitrate salts **2** and **3** (pure) as well as mixtures of **2** with 1:1 mixtures with DNAN, TNT and RDX.

by a possible phase transition. Melting of **2** could not be observed and was proven by heating in a melting apparatus. The dinitrate salt is less stable toward temperature. Exothermic decomposition was observed above 155°C. Both compounds are compatible with aluminum.

We also looked for compatibilities of **2** in 1:1 mixtures with DNAN (2,4-dinitroanisole), TNT (2,4,6-trinitrotoluene) and RDX. In the case of the RDX mixture, only the decomposition point of RDX can be observed at >205°C. In the thermo plots of the TNT and DNAN mixtures, the corresponding melting points of TNT (78–80°C) and DNAN (94–96°C) can be observed. Decomposition could not be observed below temperatures of 190°C.

In the following, the energetic properties of **2** and **3** are described. The impact and friction sensitivities were measured using a BAM drop hammer [13] and BAM friction tester [13], respectively. A comparison of their energetic properties with those of the compounds presented in Fig. 5 is shown in Tables 2 and 3.

For better comparison, all heats of formation were calculated with the atomization method using CBS-4 M-based electronic enthalpies. The gas-phase enthalpies of formation were either converted to the solid-state enthalpies by Trouton's rule [14] or by subtracting the lattice enthalpies theoretically calculated by Jenkins' equations [15]. All densities were adopted from X-ray measurements at low temperatures.

The detonation parameters were calculated with the EXPLO5.05 computer code [16] using the calculated heats of formation and the crystal densities.

Compared to other low-sensitivity explosives, **2** shows a great thermal stability of 276°C. Its impact sensitivity (plate shaped crystals, 100- to 500-μm grain size) of 11 J is lower than that of RDX and slightly higher than that of the other compounds listed in Table 2. However, no experiments regarding the crystal morphology have been performed. **2** Is insensitive toward friction (360 N). Except for FOX-7, TNGU, and RDX, **2** has the highest calculated detonation velocity (8,655 m s^{-1}) of the compounds shown in Scheme 2. We also tried to measure the experimental detonation velocity of **2** using the optical fiber method [17]. Loading densities between 1.3 and 1.5 g cm^{-3} could be achieved. The obtained velocities of detonation initiated by a commercially available detonator (DYNADET C2-25MS, Orica, Victoria, Australia) were between 6,877 and 7,401 m s^{-1}, which were also calculated to be in the expected range (for these loading densities) by the EXPLO5 code [17]. The explosiveness of **2** has also been evaluated using a small-scale shock reactivity test [18], which was introduced by researchers at Indian Head Division, Naval Surface Warfare Center. **2** Could be initiated using a commercially available detonator (DYNADET C2-25MS). The dent obtained was slightly smaller than that of RDX. **3** Is more sensitive than **2** and has an impact sensitivity of 7 J and a friction sensitivity of 200 N. Looking at the calculated performance of **3**, the compound had a a V_{det} of 8,594 m s^{-1} and a detonation pressure of 331 kbar, comparable to **2**, despite having a much higher density of 1.945 g cm^{-3} and a better oxygen balance of 0%. This can be explained by the lack in heat of formation, which is caused by the additional mass of a nitrate ion and the additional lattice enthalpy caused by it.

In addition to low cost and high thermal stability, **2** and **3** show another outstanding property. The compounds burn completely smokeless and are therefore suitable as ingredients in smokeless gun or rocket propellants. The specific impulse assuming a chamber pressure of 60 bar of **2** and **3** calculated with EXPLO5.05 was 230 and 220 s, respectively. Mixtures with aluminum showed even higher calculated specific impulses.

Table 2 Results of heat of formation calculation (based on CBS-4M values)

Compound	Formula	FW (g mol^{-1})	$-E$ (H)	T_m (%)	T_{dec} (°)	$\Delta_f H(g)$ (kJ mol^{-1})	$\Delta_{sub}H/\Delta_L H^a$ (kJ mol^{-1})	$\Delta_f H_m^\circ$ (kJ mol^{-1})	dn	$\Delta_f U^\circ$ (kJ kg^{-1})
TATB	$C_6H_6N_6O_6$	258.15	1,010.586919	350	350	11.4	117.2	−105.7	9	−323.1
ANTA	$C_2H_3N_5O_2$	129.08	501.483526	238 [28]	241	188.8	96.1	92.7	5	814.2
DINGU	$C_4H_4N_6O_6$	232.11	933.376594	—	225 [29]	−188.2	93.7	−281.9	8	−1,128.9
TNGU	$C_4H_2N_8O_{10}$	321.99	1,341.868154	200	>200	48.8	89.0	−40.2	10	−47.8
2,4-DNI	$C_3H_2N_4O_4$	158.07	634.459216	264	270	108.0	100.9	7.1	5	123.0
FOX-7	$C_2H_4N_4O_4$	148.08	597.604182	—	235	13.3	95.6	−82.3	6	−455.1
FOX-12	$C_2H_7N_7O_5$	209.12	—	—	215	254.4[b]	511.4[a]	−257.1	9.5	−1,116.5
NTO	$C_2H_2N_4O_3$	130.06	521.361307	265 [30]	270 [31]	−16.5	101.2	−117.7	4.5	−819.1
LLM-105	$C_4H_4N_6O_5$	216.11	858.170558	—	342	126.7	115.6	11.1	7.5	137.0
2	$C_2H_7N_5O_5$	181.11	—	—	273	236.9[b]	536.4[a]	−299	8.5	−1,537
3	$C_2H_8N_6O_8$	244.12	—	—	155	925.9[b]	1724.3	−798.4	11	−3,158.2
RDX	$C_3H_6N_6O_6$	222.12	896.346781	205 [32]	210 [32]	176.2	89.9	86.3	9	489.0

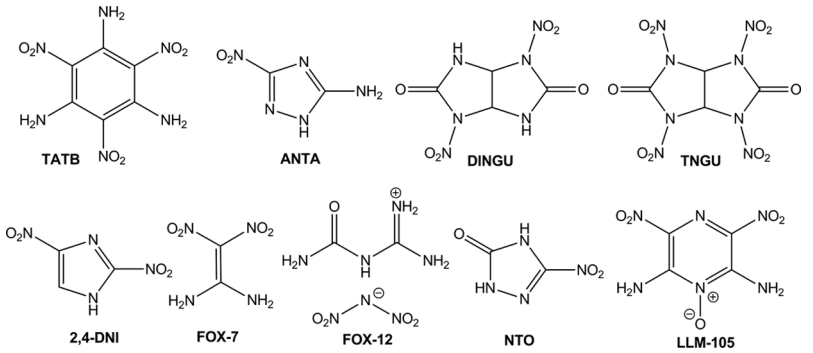
[a]Lattice enthalpy.
[b]Gas phase enthalpies of formation of the ionic compounds are taken as the respective sums of the noninteracting component ions.

Table 3 Energetic properties of **2** and **3** in comparison with prominent low sensitive explosives

Compound	IS (J)[a]	FS (N)[b]	Ω (%)[c]	ρ (g cm^{-3})[d]	$-\Delta_{Ex}U^{\circ}$ (kJ kg^{-1})[e]	T_{det} (K)[f]	P_{CJ} (kbar)[g]	$V_{Det.}$ (m s^{-1})[h]	V_o (L kg^{-1})[i]
TATB	50 [32]	>360 [32]	−55.78	1.93 [2]	4,625	3,297	312	8,335	640
ANTA	35 [32]	>360	−43.38	1.819 [3]	4,313	3273	287	8,281	736
DINGU	18 [29]	250 [29]	−27.57	1.992 [4]	4,206	3,306	331	8,364	661
TNGU	25 [5]	194 [5]	4.97	2.00 [5]	5,482	4,474	378	8,779	659
2,4-DNI	>25 [33]	140	−30.36	1.77 [6]	5,183	4,021	279	7,938	635
FOX-7	12–14	340 [34]	−21.61	1.907 [7]	5,306	3,758	363	8,827	741
FOX-12	>30	>360	−22.08	1.775* [35]	5,067	3,471	316	8,591	827
NTO	71	>360	−24.60	1.926 [36]	3,967	3,237	301	8,167	683
LLM-105	18–30	>360	−37.01	1.92 [37]	4,935	3,676	333	8,482	660
2	11	>360	−22.08	1.84	4,661	3,275	325	8,655	827
3	7	200	0	1.945	3,978	3,042	331	8,594	825
RDX	7.4 [32]	120 [32]	−21.61	1.858 [38]	6,190	4,232	380	8,983	734

[a]Impact sensitivity (BAM drop hammer; one of six).
[b]Friction sensitivity (BAM friction tester; one of six).
[c]Oxygen balance related to CO_2 [$\Omega = (xO - 2yC - 1/2z\mathrm{H})M/1600$].
[d]Density from X-ray diffraction.
[e]Energy of explosion.
[f]Explosion temperature.
[g]Detonation pressure.
[h]Detonation velocity.
[i]Volume of detonation gases (assuming only gaseous products).
[e–i]Calculated with EXPLO5.05 [16].
*U. Bemm (personal communication) and CCDC (Cambridge Crystallographic Data Centre) No. 143181.

Lastly, the aquatic toxicity of **2** was investigated by the luminescent bacteria inhibition test. Many explosives such as TNT, CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) [19], and RDX have been shown to be toxic [20] to vital organisms at the base of the food chain. In addition, RDX is a probable human carcinogen [21]. To assess the toxicity of OHN to aquatic life, diluted aqueous solutions of the explosive were subjected to the luminescent marine bacterium *Vibrio fischeri* using the commercially available bioassay system LANGE LUMIStox [22]. *Vibrio fischeri* is a representative species for other aquatic life and therefore is a useful indicator when it comes to groundwater pollution. As the most important toxicological parameter, the EC_{50} value of the sample was determined. EC_{50} is the effective concentration of the examined compound, at which the bioluminescence of the strain *Vibrio fischeri* is decreased by 50% after a defined period of exposure compared to the original bioluminescence of the sample



Scheme 2. Prominent low-sensitivity explosives: TATB (1,3,5-triamino-2,4,6-trinitrobenzene), ANTA (3-amino-5-nitrotriazole), DINGU (1,4-dinitrotetrahydroimidazo[4,5-d]imidazole-2,5-(1H,3H)-dione), TNGU (tetranitroglycoluril), DNI (2,4-dinitroimidazole), FOX-7 (1,1-dinitro-2,2-diaminoethene), FOX-12 (guanylurea dinitramide), NTO (nitro-triazolone), and LLM-105 (3,5-dinitro-2,6-pyrazinediamine 1-oxide).

before being treated with the differently diluted solutions of the test compound. For RDX we observed an EC_{50} value of 91 ppm. The EC_{50} value after an incubation time of 30 min of OHN was determined to be 1,240 ppm. This was much lower than the EC_{50} value found for RDX, indicating a lower toxicity toward aquatic life.

Experimental Part

The crystal structure was determined on an Oxford Diffraction (Abingdon, UK) Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using a $\lambda_{MoK\alpha}$ radiation wavelength of 0.71073 Å at − 100°C. Data collection and data reduction were carried out using CrysAlisPro software [23]. The structure was solved with SIR-92 [24] refined with SHELXL-97 [25] and finally checked using the PLATON software [26] integrated in the WINGX software suite [27]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorption was corrected by a SCALE3 ABSPACK multiscan method (empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm) [23].

All reagents and solvents were used as received (Sigma-Aldrich, Munich, Germany; Fluka, Munich, Germany; Acros Organics, Geel, Belgium) if not stated otherwise. Melting and decomposition points were measured with a Linseis PT10 DSC (Selb, Germany) using heating rates of 5°C min^{-1}, which were checked with a Büchi (Essen, Germany) melting point B-450 apparatus. ^{1}H-, ^{13}C-, and ^{15}N-NMR spectra were measured with a JEOL 400 MHz instrument (Tokya, Japan). All chemical shifts are provided in parts per million relative to tetramethylsilane (TMS) (^{1}H, ^{13}C) or nitromethane (^{15}N). Infrared spectra were measured with a Perkin-Elmer Spektrum One FT-IR instrument (Waltham, MA, USA). Raman spectra were measured with a Perkin-Elmer Spektrum 2000 R NIR FT-Raman instrument equipped with an Nd:YAG laser (1,064 nm). Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer (Selb, Germany).

Oxalyldihydrazide (1)

To a solution of 6 mL (124 mmol) hydrazine hydrate in 100 mL ethanol, 7.31 g (50 mmol) of diethyl oxalate was added dropwise. The precipitate was isolated by filtration, washed with ethanol, and dried in air, yielding 5.73 g (97%) of colorless product. DSC (5°C min^{-1}): 236°C (mp), 245°C (dec.); IR (atr, cm^{-1}): $\tilde{\nu} = 3284$ (m), 3180 (w), 1646 (m), 1579 (m), 1531 (s), 1421 (w), 1319 (w), 1293 (w), 1255 (s), 1124 (s), 952 (vs), 828 (s), 718 (vs); Raman (1,064 nm, 300 mW, 25°C, cm^{-1}): $\tilde{\nu} = 1770$ (6), 1572 (5), 1472 (8), 1357 (4), 1279 (18), 1124 (4), 1098 (3), 1024 (4), 935 (100), 793 (49), 638 (24), 627 (12), 473 (17), 458 (14); ^{1}H-NMR (DMSO-d_6, 25°C, ppm) δ: 9.93 (2H), 4.47 (4H); ^{13}C-NMR (DMSO-d_6, 25°C, ppm) δ: 158.4; EA ($C_2H_6N_4O_2$, 118.09). Calc.: C, 20.34; H, 5.12,; N, 47.44%; found: C, 20.59; H, 4.90; N, 47.53%.

Oxalyldihydrazinium Nitrate (2)

1.18 g (10 mmol) oxalyldihydrazide was dissolved in a hot mixture of 5.5 mL 2 M HNO_3 and 10 mL water. The solution was poured into 20 mL of ice-cold ethanol, yielding 1.80 g (99%) of colorless crystalline **2**. DSC (5°C min^{-1}): 273°C (dec.); IR (atr, cm^{-1}): $\tilde{\nu} = 3307$ (w), 3178 (w), 3028 (w), 2775 (w), 1674 (m), 1531 (m), 1326 (s), 1243 (s), 1152 (w), 1088 (w), 995(m), 802 (m), 709 (m); Raman (1064 nm, 300 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3224$ (4), 1735 (9), 1703 (15), 1584 (12), 1553 (28), 1346 (19), 1289 (23), 1206 (9), 1094 (10), 1049 (100), 1003 (4), 938 (15), 812 (2), 719 (7), 510 (5), 400 (5); ^{1}H NMR (DMSO-d_6, 25°C, ppm) δ: 8.28 ^{13}C{^{1}H} NMR (DMSO-d_6, 25°C, ppm) δ: 157.8; EA ($C_2H_7N_5O_5$, 181.11): calc.: C 13.26, H 3.90, N 38.67%; found: C 13.50, H 3.74, N 38.59%; BAM drophammer: 12 J; friction tester:>360 N; ESD: 0.3 J.

Oxalyldihydrazinium Dinitrate (3)

Oxalyldihydrazide, 2.36 g (20 mmol), was dissolved in 10 mL of boiling 30% nitric acid. The solution was cooled to room temperature and crystallization was completed by the addition of 20 mL cold ethanol; 4.88 g (100%) of colorless **3** was isolated by filtration. DSC (5°C min^{-1}): 155°C (dec.); IR (atr, cm^{-1}): $\tilde{\nu} = 3052$ (m), 2699 (w), 1687 (s), 1567 (m), 1533 (s), 1340 (vs), 1256 (s), 1202 (s), 1174 (s), 1047 (m), 1026 (w), 815 (s), 729 (w); Raman (1,064 nm, 200 mW, 25°C, cm^{-1}): $\tilde{\nu} = 3050$ (18), 1719 (19), 1559 (10), 1214 (9), 1123 (11), 1052 (100), 927 (11), 732 (10); ^{1}H-NMR (DMSO-d_6, 25°C, ppm) δ: 10.58; ^{13}C{^{1}H}-NMR (DMSO-d_6, 25°C, ppm) δ: 157.3; EA ($C_2H_8N_6O_8$, 244.12). Calc.: C, 9.84; H, 3.30; N, 34.43%; found: C, 9.76; H, 3.41; N, 33.22%; BAM drop hammer: 7 J; friction tester: 200 N; ESD:>1.5 J.

Conclusions

From this initial study the following conclusions can be drawn:

- Oxalylhydrazinium nitrate (OHN, **2**) and oxalylhydrazinium dinitrate (OHDN, **3**) were synthesized and intensively characterized. The crystal structures of OHN and OHDN were determined. Both new organic nitrate salts could be used in high-energy applications and also as ingredients for propellant compositions.
- OHN is less sensitive than RDX and OHDN is of comparable sensitivity to RDX. OHN and OHDN can be easily and cost-effectively synthesized in large scales and excellent yields. The lab-scale costs were calculated to be $40 per kilogram of OHN.

The thermal stability of OHN is much greater than that of RDX. Thermal studies of mixtures of OHN with TNT, DNAN, and RDX showed compatibility up to 180°C.

Acknowledgments

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Energetic Materials

Dense Energetic Nitraminofurazanes

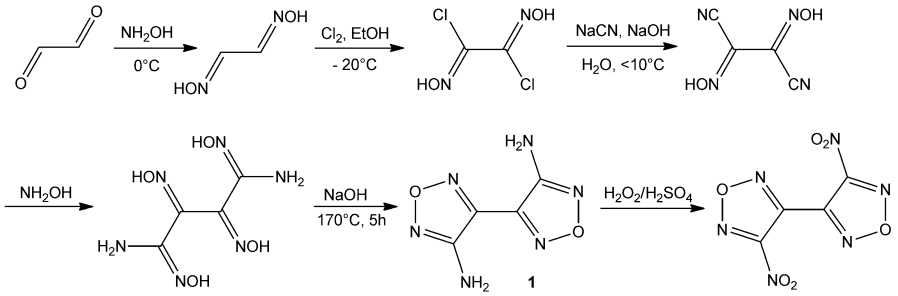
Dennis Fischer, Thomas M. Klapötke,* Marius Reymann, and Jörg Stierstorfer[a]

Abstract: 3,3′-Diamino-4,4′-bifurazane (**1**), 3,3′-diaminoazo-4,4′-furazane (**2**), and 3,3′-diaminoazoxy-4,4′-furazane (**3**) were nitrated in 100% HNO_3 to give corresponding 3,3′-dinitramino-4,4′-bifurazane (**4**), 3,3′-dinitramino-4,4′-azofurazane (**5**) and 3,3′-dinitramino-4,4′-azoxyfurazane (**6**), respectively. The neutral compounds show very imposing explosive performance but possess lower thermal stability and higher sensitivity than hexogen (RDX). More than 40 nitrogen-rich compounds and metal salts were prepared. Most compounds were characterized by low-temperature X-ray diffraction, all of them by infrared and Raman spectroscopy, multinuclear NMR spectroscopy, elemental analysis, and by differential scanning calorimetry (DSC). Calculated energetic performances using the EXPLO5 code based on calculated (CBS-4M) heats of formation and X-ray densities support the high energetic performances of the nitraminofurazanes as energetic materials. The sensitivities towards impact, friction, and electrostatic discharge were also explored. Additionally the general toxicity of the anions against *vibrio fischeri*, representative for an aquatic microorganism, was determined.

Introduction

The term "high-energy dense materials" (HEDM) comprises basically three classes of energetic materials such as 1) propellants, 2) explosives, and 3) pyrotechnics. The research towards materials for all classes is an ongoing project in many research groups world-wide. The challenge is based on the combination of the three main demands 1) performance, 2) safety, and 3) practicability. Regarding secondary explosives important values to describe performances, for example, are solid state density (ρ), detonation pressure (p_{CJ}), and velocity (V_{det}), heat of formation ($\Delta_f H^\circ$), and energy of explosion (U_{exp}). Safety is related to sensitivities (impact, friction, and electrostatic discharge), thermal and long-term stability, as well as compatibilities. The term practicability includes, for example, potential large scale syntheses, yields, and synthetic costs and crystallization processes.

A wide variety of aminofurazanes are known in the field of energetic materials due to their stability and high heats of formation. One of the most important and most readily accessible are 3,3′-diamino-4,4′-azofurazane (**2**), and 3,3′-diamino-4,4′-azoxyfurazane (**3**), which can be easily prepared from 3,4-diaminofurazane by using either hypochlorite or oxone in aqueous solution.[1] Both have been tested for their suitability as insensitive explosives.[2] 3,3′-Diamino-4,4′-bifurazane (**2**) is available from dichloroglyoxime through dicyanoglyoxime and tetraoximodiaminobutane[3] but also in a one-pot synthesis from isocyanilic acid.[4] Although the compounds have been extensively investigated concerning their oxidation to nitrofurazanes[5] (Scheme 1) and azo/azoxyfurazanes,[6–10] only diaminoazofurazane (**2**) has been nitrated so far.[11]



Scheme 1. Synthesis towards 3,3′-dinitro-4,4′-bifurazane.[3]

Results and Discussion

As depicted in Scheme 2, the nitraminofurazanes were synthesized by nitration of the corresponding aminofurazanes in 100% HNO_3 at 0–5 °C for 1 h. Quenching of the nitration reactions with ice-water caused the nitraminofurazanes to precipi-

[a] D. Fischer, Prof. Dr. T. M. Klapötke, M. Reymann, Dr. J. Stierstorfer
Department of Chemistry, Energetic Materials Research
Ludwig Maximilian University
Butenandtstrasse 5–13, 81377 München (Germany)
Fax: (+49) 89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

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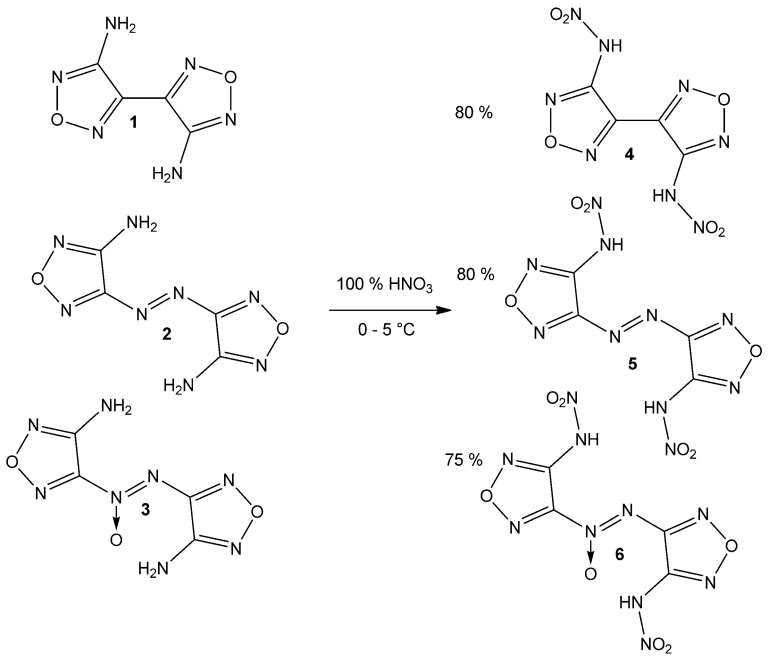


Scheme 2. Synthesis of 3,3′-dinitramino-4,4′-bifurazane (**4**), 3,3′-dinitramino-4,4′-azofurazane (**5**), and 3,3′-dinitramino-4,4′-azoxyfurazane (**6**).

tate in 75 to 80% yield. The yields can be improved to over 90% by extraction of the filtrate with organic solvents like ethyl acetate. Various metal salts and salts formed with energetic cations were synthesized by deprotonation of the nitramines with the corresponding bases in aqueous or alcoholic solution (Schemes 3–5).

Crystal structures

During this work the crystal structures of compounds **1**, **4**, **6**–**20**, **23**, **25**, **32**–**34**, **37**, **39**, and **40** were determined by low-temperature X-ray diffraction. Selected data and parameters from the low-temperature X-ray data collection and refinements are given in the Supporting Information (Tables S1–S4). Further information regarding the crystal-structure determinations have been deposited with the Cambridge Crystallographic Data Centre (CCDC).[12]

3,3′-Diamino-4,4′-bifurazane (**1**) crystallizes in the triclinic space group *P*-1 with one molecule in the unit cell. The density at a temperature of 100 K is 1.789 g cm^{-3}. The molecule, shown in Figure 1, is nearly planar ($<$C1-C2-C2^{i}-N2^{i} = 0.4(2)°. Also the N–H protons are almost in the ring plane ($<$H3B-N3-C1-N1 = 5.8(14)°). Nitrogen atom N3 therefore behaves like a sp^2 center. This can also be seen by the C1–N3 bond length (1.347(2) Å), which is significantly shorter than a C–N single bond (1.47 Å).

4,4′-Dinitramino-3,3′-bifurazane (DNABF, **4a**) crystallizes from methanol, without inclusion of solvent molecules, in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Figure 2 illustrates the molecular unit. All chemical bonds in the DNABF molecule exhibit typical bond lengths of aromatic furazane rings and nitramines, as expected. Only a distortion of the two furazane rings to each other can be observed, which is indicated by a torsion angle N2-C2-C3-N5 of 157.43(13)°. Moreover, the fur-

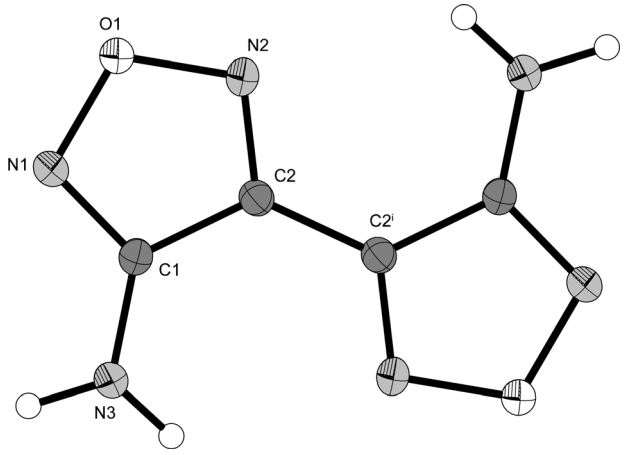


Figure 1. Molecular structure of **1**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry code: (i) 1−*x*,−*y*, 1−*z*.

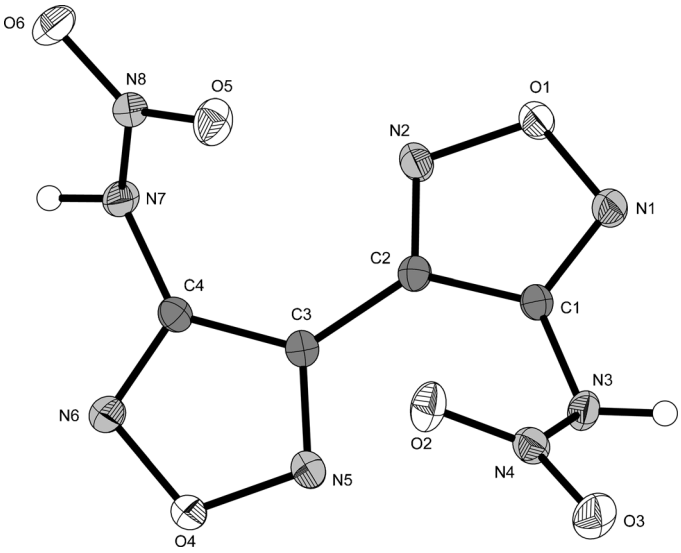
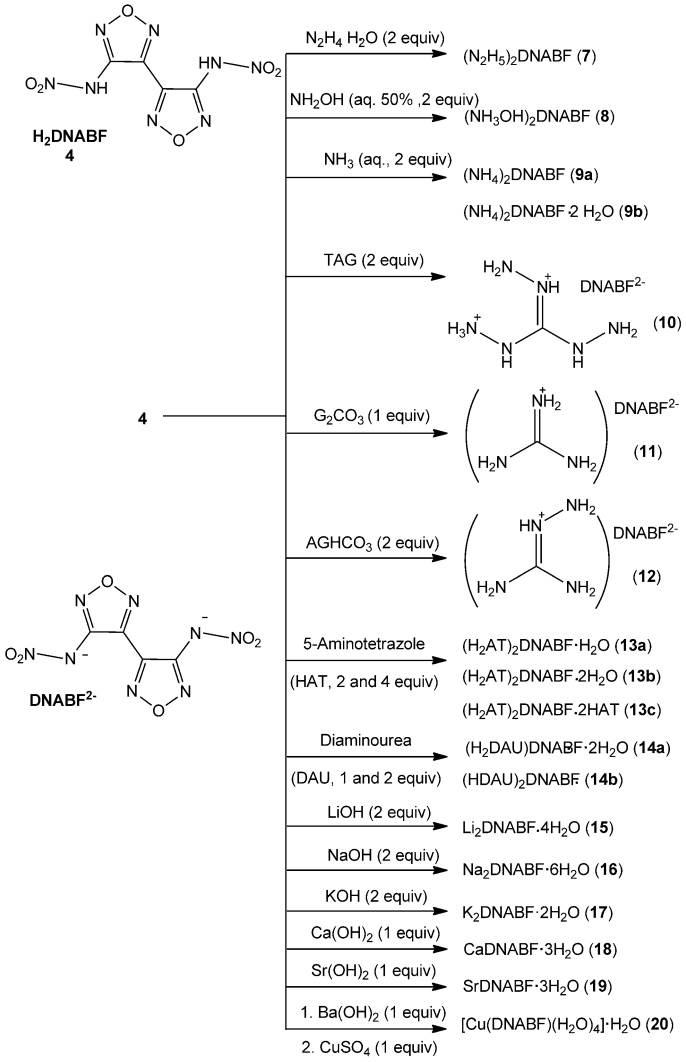


Figure 2. Representation of the molecular unit of **4a**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.



Scheme 3. Synthesis of the salts **7**–**20** of dinitramino-bifurazane (**4**) in water. G = guanidine; AG = aminoguanidine; TAG = triaminoguanidine.

azane rings reveal a *cis* position of their nitramino groups. DNABF is comprised of a very dense packed structure (1.978 g cm^{-3}).

A monoclinic ($P2_1/n$) low density (1.936 g cm^{-3}) polymorph **4b** of **4** was obtained from a mixture of **4** and $[Ca(NO_3)_2]\cdot 4H_2O$ in water which is shown in Figure 3. Whereas the structure of **4a** showed a *cis* positioning of the nitramino groups, the nitramino groups in this polymorph are posted in the *trans* position, opposite to each other. In this structure the furazane rings are planar to each other.

3,3′-Dinitramino-4,4′-azoxyfurazane (**6**) crystallizes anhydrously with a density of 1.915 g cm^{-3} in the orthorhombic space group $P2_12_12_1$ and with four molecules per unit cell. The molecular unit is shown in Figure 4.

With respect to potential practical applications one of the most promising compounds is bis(hydrazinium) 3,3′-dinitramino-4,4′-bifurazane (**7**), which crystallizes anhydrously from methanol in the monoclinic space group $P2_1/n$ with a density of 1.812 g cm^{-3} and two molecular moieties in the unit cell. The torsion angle C1-C2-C2^{i}-C1^{i} (180°) and also O2-N4-N3-C1 (1.38(19)°) of the nitramino groups, demonstrate that the DNABF dianion is nearly planar. The N5-N6/N5^{i}-N6^{i} bond length (1.445(2) Å) of the two hydrazinium cations is in the range of a typical N–N single bond. Moreover, the cations form two hydrogen bonds, one strong H-bond of 1.873(23) Å (O3···H6B) and one bifurcated H-bond of 2.549(19) Å (N1^{i}···H5B) and of 2.485(22) Å. Figure 5 represents the molecular unit of **7**.

Bis(hydroxylammonium) 3,3′-dinitramino-4,4′-bifurazane (**8**) crystallizes anhydrously from methanol in the monoclinic space group $P2_1/n$ with a very high density of 1.963 g cm^{-3} (173 K) and two molecules in the unit cell. Figure 6 illustrates the molecular unit of **8** with its hydrogen bonds between the hydroxylammonium cations and DNABF anions. The N–O bond length of the hydroxylammonium cation is in the expected range (1.415(2) Å). A bifurcated H-bond is formed between the protonated amino moiety of the cation H5B and the oxygen atom of the nitro group O3 with a bond length of 2.322(20) Å and a stronger hydrogen bond between H5B and the nitrogen atom N1 of the furazane ring with a distance of 2.159(20) Å. Another bifurcated one is

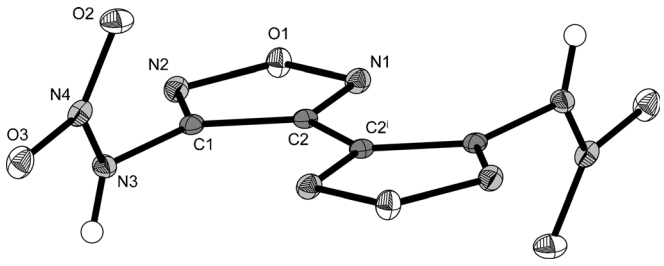


Figure 3. Representation of the low-density polymorph of **4b**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry code: (i) 1−*x*, 1−*y*, 1−*z*.

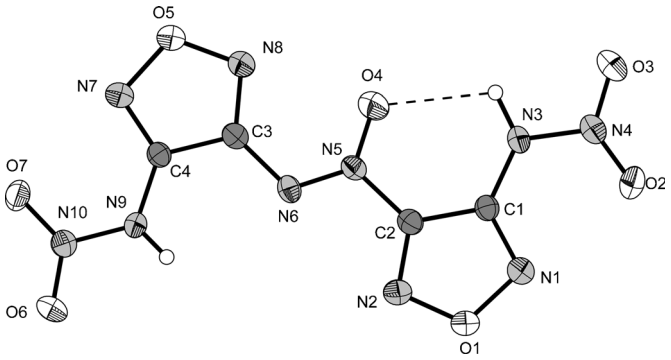
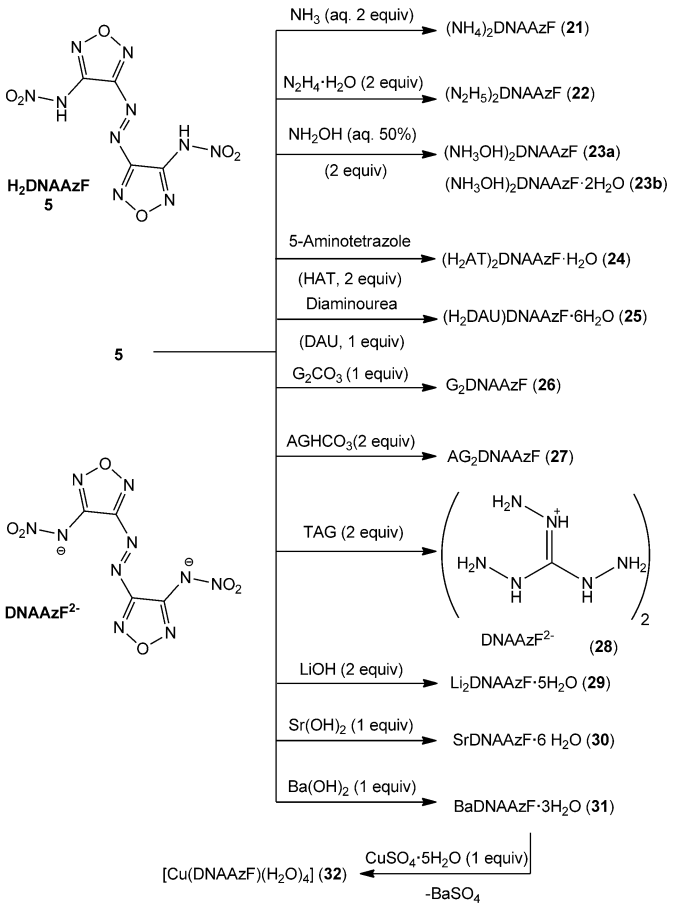
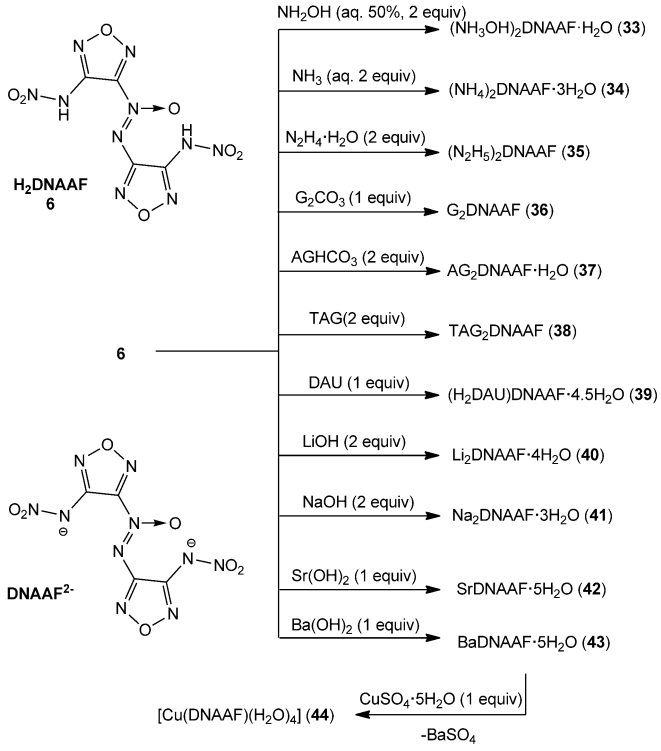


Figure 4. Molecular structure of **6**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.



Scheme 4. Synthesis of the ionic derivatives **21**–**32** of dinitraminoazobifurazane (**5**) in water. DAU = diaminourea; HAT = 5-aminotetrazole.



Scheme 5. Synthesis of ionic azoxyfurazanes **33**–**44** from dinitraminoazoxybifurazane (**6**) in water.

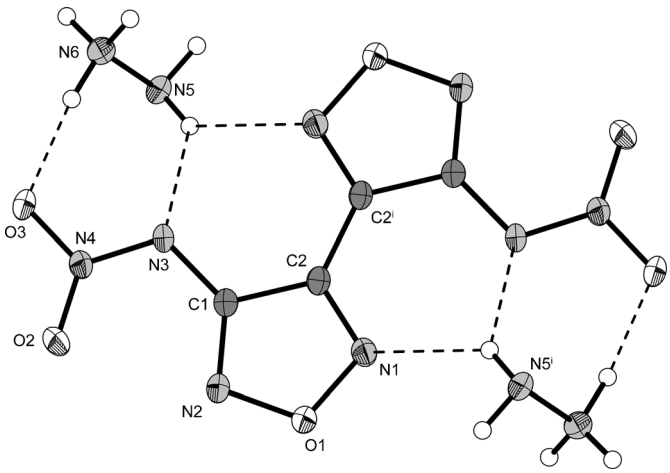


Figure 5. Representation of the molecular unit of **7**, showing the atom-labeling scheme and bond lengths (Å) with standard deviations. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry code: (i) $-x$, $-y$, $1-z$.

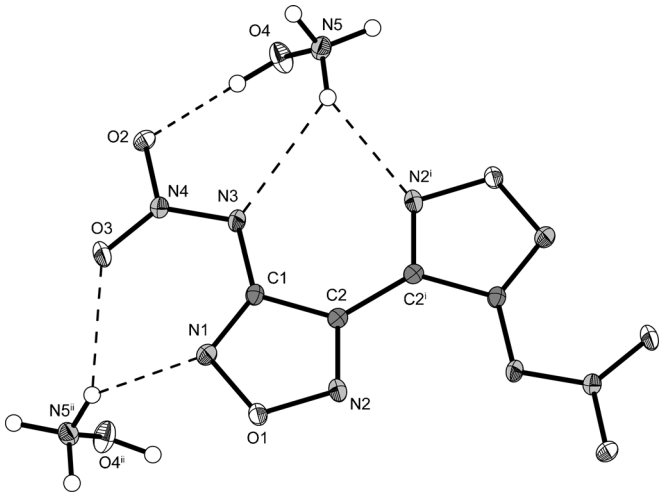


Figure 6. Representation of the molecular unit of **8**, showing the atom-labeling scheme and bond lengths (Å) with standard deviations. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry codes: (i) $2-x$, $-y$, $1-z$; (ii) $-0.5+x$, $0.5-y$, $-0.5+z$.

formed between H5C and the nitrogen atom of the nitramino group (2.525(18) Å) and also between the nitrogen atom N2^{i} of the symmetry equivalent furazane ring (2.218(18) Å). A strong hydrogen bond appears between the nitro group and the hydroxyl moiety of the cation with a distance of 1.835(21) Å (O2···H4). With an angle O2-H4···O4 of 178(2)° this H-bond can be seen as almost linear.

Bis(ammonium) 3,3′-dinitramino-4,4′-bifurazane (**9**) crystallizes anhydrously from methanol in the monoclinic space group $P2_1/n$ with a density of 1.833 g cm^{-3} and two molecules in the

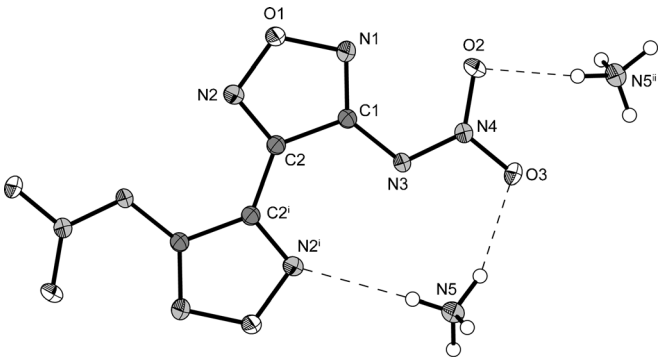


Figure 7. Molecular unit of **9**, showing the atom-labeling scheme and bond lengths (Å) with standard deviations. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $1.5-x$, $0.5+y$, $0.5-z$.

unit cell. The nitramino groups are twisted out from the annular furazane plane with a torsion angle C2-C1-N3-N4 of 170.89(19)°. In Figure 7, the main hydrogen bonds between the ammonium cations and the DNABF dianion are illustrated. One stronger H-bond occurs between the O2 oxygen atom of the nitro group and the H-bond donor N5^{ii} with a bond length at 2.147(31) Å. The other ammonium cation coordinates twice through a stronger hydrogen bond between O3 and H5D (2.056(31) Å and through a weaker one between the nitrogen atom N2^{i} of the furazane ring and H5A (2.370(31) Å). Figure 7 illustrates the coordination geometry, over hydrogen bonds, of the respective cations and anions, which lie in one plane. The ammonium cations are coordinated threefold, whereas the DNABF anions are connected through six hydrogen bonds.

Bis(hydroxylammonium) 3,3′-dinitramino-4,4′-azofurazane (**23**) crystallizes anhydrously from methanol with a density of 1.883 g cm^{-3} in the monoclinic space group $P2_1/n$ and with two molecules per unit cell. The molecular unit is shown in Figure 8. The crystal structure of the corresponding dihydrate **23 b** can be found in the Supporting Information (Figure S16).

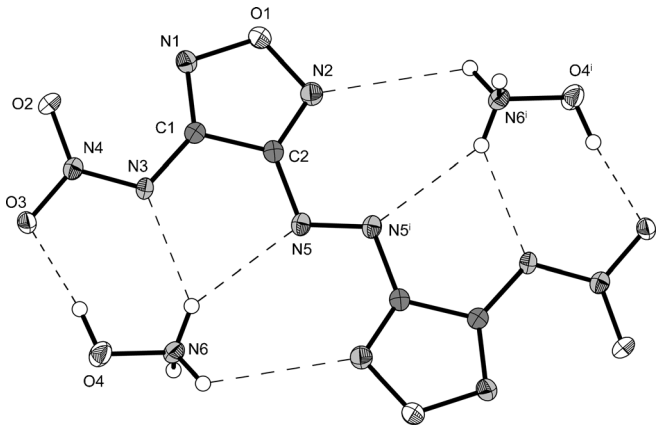


Figure 8. Molecular unit of **23 a**, showing the atom-labeling scheme and bond lengths (Å) with standard deviations. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

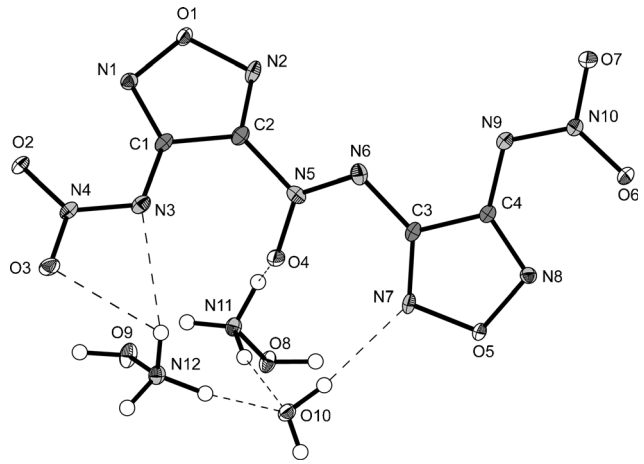


Figure 9. Molecular unit of **33**, showing the atom-labeling scheme and bond lengths (Å) with standard deviations. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

The hydroxylammonium salt of the dinitraminoazoxyfurazane **33** crystallized from methanol/ether as a monohydrate in the orthorhombic space group $P2_12_12_1$ with a high density of 1.915 g cm^{-3} and four molecules in the unit cell. Figure 9 illustrates the molecular unit of **33** with its hydrogen bonds between the hydroxylammonium cations and DNAAF anions.

The residual structures can be found in the Supporting Information.

NMR spectroscopy

All NMR spectroscopic analyses were performed in [D$_6$]DMSO. In the ^{1}H NMR spectra of **4**–**6**, the compounds show singlets at $\delta = 11.4$–11.9 ppm due to their acidic protons. The ^{13}C NMR spectrum of **4** exhibits two signals at $\delta = 153.4$ and 142.6 ppm. In ^{13}C NMR spectrum of **5** there are two signals at $\delta = 160.0$ and 147.7 ppm corresponding with the literature report.[11] Due to its unsymmetrical nature, compound **6** shows four signals in the ^{13}C NMR spectrum at $\delta = 155.6$, 153.9, 151.3, and 149.4 ppm. The ^{15}N NMR spectrum of **4** reveals four signals, at $\delta = 37.2$, 14.1, -32.4, and -198.2 ppm (Figure 10).

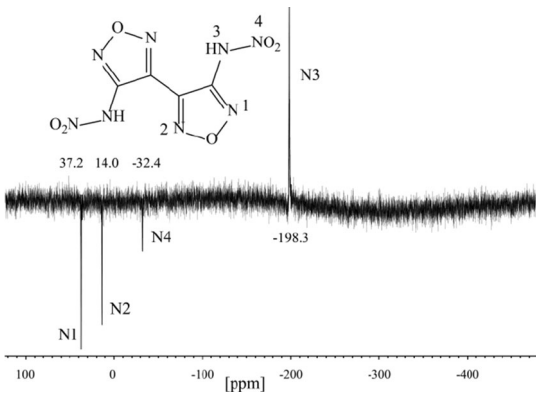


Figure 10. ^{15}N{^{1}H} NMR spectrum of **4**.

Table 1. ^{1}H NMR and ^{13}C NMR shifts of selected compounds.

Compound	^{1}H NMR δ [ppm]	^{13}C NMR δ [ppm]
1	6.49	155.9, 137.5
2	6.90	156.3, 151.2
3	6.92, 6.65	154.0, 152.6, 151.2, 148.4
4	12.22	153.1, 141.6
5	11.00	160.0, 147.7
6	14.39	155.6, 153.9, 151.3, 149.4
7	6.89	158.6, 142.3
8	9.98	158.7, 142.2
9	7.12	158.7, 142.3
10	8.56, 4.32	159.4, 158.8, 142.3
11	6.92	158.8, 158.4, 142.3
12	8.53, 7.20, 6.67, 4.65	159.3, 158.8, 142.3
21	7.13	160.3, 153.0
22	8.32	160.4, 153.2
23	10.05	160.4, 153.1
24	10.40	160.1, 155.6, 148.3
25	9.69, 4.63	160.3, 157.3, 152.6
26	6.91	160.5, 158.4, 153.0
27	8.56, 7.23, 6.73, 4.68	160.5, 159.3, 153.0
28	8.55, 4.58	159.5, 154.0, 150.6
33	10.08	155.6, 155.2, 154.2, 151.7
34	7.12	155.6, 155.4, 154.3, 151.7
35	7.09	155.6, 155.4, 154.4, 151.7
36	6.87	158.4, 155.6, 155.5, 154.4, 151.8
37	8.52, 7.21, 6.69, 4.64	159.3, 155.6, 155.5, 154.4, 151.8
38	8.55, 4.44	159.6, 155.6, 155.3, 154.3, 151.7
39	9.81, 4.02	157.2, 155.6, 154.8, 154.3, 151.7

The carbon signals of the salts of **4**–**6** are shifted to lower fields in comparison with the acids. In particular, the carbon atoms connected to the nitramines are shifted to lower field up to $\delta = 6$ ppm. No irregularities in the ^{1}H/^{13}C NMR chemical shifts of the nitrogen-rich cations were observed. All ^{1}H/^{13}C NMR chemical shifts of compounds **1**–**12**, **21**–**28**, and **33**–**39** are listed in Table 1. The values of compounds **5** and **21** are in good agreement with the literature.[11]

Physicochemical properties

Since all materials investigated are highly energetic compounds, their energetic behaviors were investigated.

Thermal behavior

The thermal behavior of compounds **4**–**27** were investigated on a Linseis PT10 DSC with a heating rate of 5 °C min^{-1} using approximately 1.5 mg of material. The nitramines **4** and **6** show poor thermal stability of 80 (**4**) and 70 °C (**6**), respectively. According to the literature,[11] compound **5** decomposes at 122 °C. The salts of **4**–**6** show increased thermal stabilities up to 280 °C (**11**). The guanidinium salts show the highest thermal stabilities of all the salts. The azo and azoxy-bridges between the nitraminofurazanes reduce the thermal stability. For comparison, guanidinium salts **18** and **25** already decompose at 242 and 255 °C, respectively. DSC plots of compounds **4**, **6**–**8**, **11**, **26**, and **36** are depicted in Figure 11.

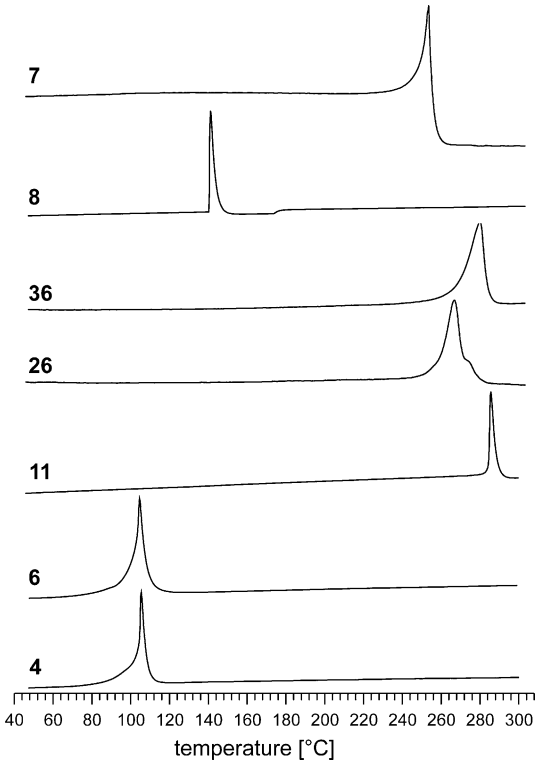


Figure 11. DSC plots of compounds **7**, **8**, **36**, **26**, **11**, **6**, and **4** (top to bottom).

Heats of formation, sensitivity and detonation parameters

Heats of formation were calculated theoretically using the atomization Equation (1) and CBS-4M electronic enthalpies.

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma \Delta_f H^\circ_{(atoms,298)} \quad (1)$$

The detonation parameters were calculated with the EXPLO5.05 computer code using X-ray densities, which were converted to room-temperature values according to Equation (2). A coefficient of volume expansion[13] α_v of 1.5×10^{-4} K^{-1} was used.

$$\rho_{298K} = \rho_T / (1 + \alpha_v (298 - T_0)) \quad (2)$$

For a complete discussion on the methods used please see the Supporting Information. Only the physicochemical properties of compounds **4**–**12**, **14b**, and **23a** are discussed because they are CHNO compounds and anhydrous crystal structures were obtained or known in the literature.[11] The energetic parameters in comparison with RDX (cyclotrimethylene-trinitramine) are summarized in Tables 3 and 4 (see the Experimental Section); all compounds are formed endothermically. Generally the azo-bridged compounds have more positive energies of formation than the C–C bridged bis-nitraminofurazanes; the highest value was calculated for **5** ($\Delta_f U^\circ = 2957$ kJ kg^{-1}), whereas the azoxy bridge leads to a slight decrease (($\Delta_f U^\circ$ (**6**) = 2634 kJ kg^{-1}). The neutral compounds **4**–**6** are very powerful explosives due to their 1) high energy of formation 2) good oxygen balance, and 3) very high densities. Unfortunately they

are all quite sensitive towards impact and friction and their thermal stability is low. Both aspects probably will preclude any practical use. Compound **4** shows a calculated detonation pressure (P_{CJ}) of 403 kbar and a detonation velocity (V_{det}) of 9086 m sec^{-1} at 1.5 J impact and 48 N friction sensitivity. Also **5** and **6** reach V_{det}s of above 9000 m sec^{-1} and P_{CJ}s above 400 kbar. Among the salts the hydroxylammonium salts **8** and **23a** show the highest performance values. In particular, compound **8** was calculated to have a high detonation velocity of 9363 m sec^{-1}. But again the high sensitivities of **23a** and the low decomposition temperatures of **8** and **23a** may limit their applicability in the field of high-performing explosives. The most mechanically and also thermally insensitive salt is **11** (IS > 40 J, FS > 360 N, T_{dec} 280 °C). These values allow compound **11** to be classified as insensitive material. Regrettably the calculated explosive power of 271 kbar and 8225 m sec^{-1} is below that of RDX. The most suitable salt for any application (explosive and propellant formulations) is **7**, which decomposes not before 230 °C, is moderately sensitive towards mechanical stimuli (IS 6 J, FS 120 N). It has similar calculated performance values (V_{det} = 9058 m sec^{-1}, P_{CJ} = 354 kbar) to RDX (V_{det} = 8983 m sec^{-1}, P_{CJ} = 380 kbar). For this reason a thermogravimetric analysis of **7** was performed. The TGA (the Supporting Information) shows that **7** starts to lose weight not before 200 °C (heating rate of 2 K min^{-1}). Its decomposition released mainly gaseous products (solid residue only five weight percent of the original material).

Toxicity assessment

To determine the toxicity of the nitraminofurazane salts in general, the bis(ammonium) salts (**9**, **21**, and **34**) were tested, due to their almost non-toxic cation. Liquid-dried luminescent bacteria of the strain *Vibrio fischeri* NRRL-B-11177 obtained from HACH LANGE GmbH (Düsseldorf, Germany) were used for the luminescent bacteria inhibition test. A 2% NaCl stock solution was prepared prior to the measurements using HPLC-grade water to ensure optimal salt conditions for the bacteria. The tested compounds of a known weight were diluted in this stock solution and, after complete dissolution, were adjusted to a final volume. Dilutions were prepared out of these solutions corresponding to DIN/EN/ISO11348 without G1 level. RDX was first dissolved in acetone and then diluted in 2% NaCl stock solution to obtain a 1% (vol%) acetone concentration for each dilution. A 1% acetone concentration is not toxic to *vibrio fischeri*.[26] The measurements were performed on a LUMIStox 300 spectrometer obtained by HACH LANGE GmbH (Düsseldorf, Germany) and were carried out as described by the provider at 15 °C.

Generally, the here-determined parameter EC_{50} is the effective concentration, at which the bioluminescence of the used bacteria strain is decreased by 50% after a defined period of exposure as compared with the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound. Each sample was tested after 15 and 30 min. The EC_{50} values after 15 and 30 min were calculated with the HACH-LANGE LUMISsoft IV provided by the HACH LANGE GmbH (Düsseldorf, Germany).

Table 2. Experimental data of EC_{50} values of compounds **9**, **21**, and **34** compared to commonly used energetic compounds.

Compound	EC_{50} (15 min) [g L^{-1}]	EC_{50} (30 min) [g L^{-1}]
Sodium azide	0.254	0.177
Sodium nitrotetrazolate	14.076	4.354
RDX	0.327 (0.322)[a]	0.239 (0.266)[a]
Ammonium nitrate	10.485	6.385
Ammonium perchlorate	14.582	11.143
$(NH_4)_2$DNABF (**9**)	2.884	2.795
$(NH_4)_2$DNAAzF (**21**)	0.086	0.065
$(NH_4)_2$DNAAF (**34**)	1.191	0.712

[a] Values in parentheses refer to literature-known values of RDX.[27]

As shown in Table 2, an EC_{50} value for RDX of 0.327 g L^{-1} is observed, after an incubation time of 15 min and a value of 0.239 g L^{-1} after 30 min. The herein determined EC_{50} values of $(NH_4)_2$DNABF after 15 (2.884 g L^{-1}) and 30 min (2.795 g L^{-1}) are considerably higher than the EC_{50} values found for RDX. Therefore, compound **9** and especially the DNABF anion can be seen as significantly less toxic than RDX towards *vibrio fischeri*, which is representative for other aquatic life. In contrast to **9**, $(NH_4)_2$DNAAF (**34**) is more toxic towards the bacteria and $(NH_4)_2$DNAAzF (**21**) is even more toxic than RDX.

Conclusion

3,3′-Dinitramino-4,4′-bifurazane (**4**) and 3,3′-Dinitramino-4,4′-azoxybifurazane (**6**) were synthesized for the first time by using 100% nitric acid and the corresponding amines. Nitrogen-rich and metal salts of **4**, **6**, and additionally of 3,3′-dinitramino-4,4′-azobifurazane[11] (**5**) were synthesized and characterized using X-ray single-crystal diffraction, NMR spectroscopy, IR, Raman, DSC, BAM sensitivity methods, and elemental analysis. A thermogravimetric analysis (TGA) was carried with the hydrazinium salt of **4**. Additionally the energetic properties such as heat of formation and detonation parameters of all CHNO compounds with anhydrous crystal structures were calculated. The nitraminofurazanes **4**–**6** are highly energetic and dense compounds with low decomposition temperatures. Salt formation leads to an increase of the thermal stability up to 280 °C. Very high detonation velocities were calculated especially for the hydroxylammonium salts **8** and **23a**. With respect to all the demands for new energetic materials, compound **7** could be of interest; it combines high performance with good mechanical and thermal stability. Compounds **4**–**6** are less effective as high-energy ligands in coordination chemistry. This was demonstrated by formation of the copper salts (**20**, **32**, and **44**). The anions can also be used in combination with alkali and alkaline earth metal cations for pyrotechnic colorants. The toxicity of the anions against *vibrio fischeri*, representative for aquatic microorganism, was tested and found to be

ten times less toxic than RDX for the DNABF anion but considerably more toxic for the DNAAzF and DNAAF anions.

Experimental Section

General procedures

Raman spectra were recorded with a Bruker MultiRAM FT-Raman fitted with a liquid-nitrogen-cooled germanium detector and a Nd:YAG laser ($\lambda = 1064$ nm), infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature, the samples were solids. NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^1H, 400.2 MHz; ^{13}C, 100.6 MHz), $MeNO_2$ (^{14}N, 40.7 MHz). Elemental analysis (C,H,N) were performed with a Elementar Vario EL analyzer. Decomposition points were determined by differential scanning calorimetry (DSC) measurements with a Linseis DSC-PT10, using a heating rate of 5 °C min^{-1}. Sensitivity data (impact, friction, and electrostatic discharge) were performed using a drop hammer, friction tester, and electrostatic discharge device analogous to BAM (Bundesanstalt für Materialforschung und Prüfung).[17]

XRD was performed on an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at low temperatures. The data collection and reduction was carried out using the CRYSALISPRO software.[18] The structures were solved either with SHELXS-97[19] or SIR-92[20] orSIR-97[21] refined with SHELXL-97[22] and finally checked using the PLATON[23] software integrated in the WINGX[24] software suite. All hydrogen atoms were found and freely refined. Friedel pairs of non-centrosymmetric space groups have been merged using the MERG3 command. The absorptions were corrected with a Scale3 Abspack multi-scan method.[25] The X-ray data can be obtained free of charge from The Cambridge Crystallographic Data Centre (see ref. [12] for the CCDC numbers). Tables 3 and 4 contain the energetic properties and detonation parameters. The complete Experimental Section can be found in the Supporting Information.

Table 3. Energetic properties and detonation parameters of **4**–**9a**.

	4	5	6	7	8	9a
Formula	$C_4H_2N_8O_6$	$C_4H_2N_{10}O_6$	$C_4H_2N_{10}O_7$	$C_4H_{10}N_{12}O_6$	$C_4H_8N_{10}O_8$	$C_4H_8N_{10}O_6$
F_w [g mol^{-1}]	258.11	286.12	302.12	322.20	324.17	292.17
IS [J][a]	1.5	3	1	6	11	10
FS [N][b]	48	20	16	120	288	324
ESD [J][c]	0.03	0.05	0.05	0.3	0.1	0.2
N [%][d]	43.41	48.95	46.36	52.17	43.21	47.94
Ω_{CO_2} [%][e]	−18.59	−16.77	−10.59	−34.76	−19.74	−32.85
$T_{Dec.}$ [°C][f]	80	122[11]	70	230	141	230
ρ [g cm^{-3}][g]	1.978 (173 K) 1.94 (298 K)	1.996 (110 K), 1.919(295 K)[11]	1.915(173 K) 1.88 (298 K)	1.812 (173 K) 1.78 (298 K)	1.963 (173 K) 1.93 (298 K)	1.834 (173 K) 1.80 (298 K)
$\Delta_f H_m^\circ$ [kJ mol^{-1}][h]	526	824	772	637	417	306
$\Delta_f U^\circ$ [kJ kg^{-1}][i]	2114	2957	2634	2085	1384	1149
EXPLO5.05 values:						
$-\Delta_{Ex}U^\circ$ [kJ kg^{-1}][j]	6660	7031	7104	6327	6612	5661
T_{det} [K][k]	5034	5291	5432	4205	4455	3941
P_{CJ} [kbar][l]	403	414	400	354	425	334
V_{det} [m s^{-1}][m]	9086	9255	9131	9058	9363	8748
V_o [L kg^{-1}][n]	646	664	667	794	738	759

[a] Impact sensitivity (BAM drop hammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content; [e] Oxygen balance ($\Omega = (x\mathrm{O} - 2y\mathrm{C} - 1/2z\mathrm{H})\mathrm{M}/1600$). [f] Start of decomposition temperature from DSC ($\beta = 5$ °C). [g] From X-ray diffraction, values for 298 K were calculated with $\rho_{298K} = \rho_T/(1 + \alpha_v(298 - \mathrm{T})$,[13] $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}. [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion; [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products).

Table 4. Energetic properties and detonation parameters of **10**–**12**, **14b**, **23a**, and hexogen (RDX). For footnotes [a–n] see Table 3.

	10	11	12	14b	23a	RDX
Formula	$C_5H_{10}N_{14}O_6$	$C_6H_{12}N_{14}O_6$	$C_6H_{14}N_{16}O_6$	$C_6H_{14}N_{16}O_8$	$C_4H_8N_{12}O_8$	$C_3H_6N_6O_6$
F_w [g mol^{-}]	362.22	376.25	406.28	438.33	352.18	222.12
IS [J][a]	3	40	10	40	4	7.5[14]
FS [N][b]	360	360	360	360	80	120[14]
ESD [J][c]	–	–	–	0.1	0.13	0.2
N [%][d]	54.14	52.12	55.16	51.13	4.73	37.84
Ω_{CO_2} [%][e]	−39.75	−51.02	−51.19	−40.15	−18.17	−21.61
T_{Decomp} [°C][f]	203	280	215	192	150	205
ρ [g cm^{-3}][g]	1.811 (300 K)	1.769 (100 K) 1.72 (298 K)	1.680 (173 K) 1.649 (298 K)	1.830 (100 K) 1.78 (298 K)	1.883 (173 K) 1.85 (298 K)	1.858 (90 K)[15] 1.806 (298 K)[16]
$\Delta_f H_m^\circ$ [kJ mol^{-1}][h]	584	323	580	615	718	86
$\Delta_f U^\circ$ [kJ kg^{-1}][i]	1714	964	1536	1511	2137	489
EXPLO5.05 values:						
$-\Delta_{Ex}U^\circ$ [kJ kg^{-1}][j]	5500	4744	5117	5723	6911	6190
T_{det} [K][k]	3813	3351	3523	3852	4724	4232
P_{CJ} [kbar][l]	335	271	265	333	403	380
V_{det} [m s^{-1}][m]	8836	8225	8228	8848	9273	8983
V_o [L kg^{-1}][n]	769	769	790	788	748	734

Syntheses

CAUTION! All investigated compounds are potentially explosive energetic materials, although no hazards were observed during preparation and handling these compounds. Nevertheless, this necessitates additional meticulous safety precautions (earthed equipment, Kevlar gloves, Kevlar sleeves, face shield, leather coat, and ear plugs).

3,3′-Dinitramino-4,4′-bifurazane (4): 1.01 g (6 mmol) of diaminobisfurazane were added in small portions to 100% nitric acid (8 mL) at −5–0 °C. After the addition, the solution was stirred at 0–5 °C for 45 min. The suspension was poured on 50 g of ice and the

precipitate was filtered and washed with ice-water (10 mL) and dried in air yielding 1.614 g (80%) of DNABF as a colorless solid. Another 366 mg (16%) of DNABF could be isolated upon extracting the filtrate with ethyl acetate, drying the organic phase with magnesium sulfate and evaporating the solvent. DSC (5 °C min^{-1}): 80 °C (dec.); BAM: drop hammer: 1.5 J; friction tester: 48 N; ESD: 0.03 J; IR (ATR): $\tilde{\nu}$ = 3207 (w), 1739 (m), 1622 (m), 1551 (w), 1420 (w), 1366 (w), 1304 (w), 1280 (s), 1226 (w), 1217 (w), 1088 (w), 1000 (m), 976 (w), 914 (w), 897 (w), 860 (m), 777 (vs), 745 (w), 731 (w), 705 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3218 (20), 1634 (12), 1619 (100), 1552 (98), 1454 (30), 1382 (49), 1336 (19), 1285 (32), 1033 (26), 988 (13), 913 (23), 775 (14), 749 (19), 610 (10), 491 (36), 453 cm^{-1} (12); ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 11.49 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 153.5, 141.7 ppm; elemental analysis calcd (%) for $C_4H_2N_8O_6$ (258.11): C 18.61, H 0.78, N 43.41; found: C 18.62, H 0.78, N 43.92.

3,3′-Dinitramino-3,3′-azoxybifurazane (6): Compound **3** (1.06 g, 5 mmol) was portion-wise dissolved in 100% nitric acid (6 mL) at −5–0 °C. After the addition the solution was stirred for another 45 min at 0–5 °C. The suspension was poured on 40 g of ice and the solid was filtered and dried in air yielding DNAAF (1.13 g, 75%) as a yellowish solid. Another 183 mg (12%) of DNAAF could be isolated upon extracting the filtrate with ethyl acetate, drying the organic phase with magnesium sulfate, and evaporating the solvent. DSC (5 °C min^{-1}): 70 °C (dec.); BAM: drop hammer: 1 J; friction tester: 16 N; ESD: 0.05 J; IR (ATR): $\tilde{\nu}$ = 3280 (w), 1738 (m), 1617 (s), 1521 (w), 1499 (w), 1437 (w), 1387 (m), 1362 (w), 1312 (vs), 1229 (m), 1046 (w), 1000 (w), 949 (m), 901 (w), 833 (m), 750 (m), 711 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 1592 (10), 1580 (18), 1521 (26), 1503 (100), 1468 (10), 1444 (85), 1382 (18), 1367 (65), 1324 (9), 1303 (20), 1047 (8), 871 cm^{-1} (8); ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 11.57 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C,): δ = 155.6, 153.9, 151.2, 149.4 ppm; elemental analysis calcd (%) for $C_4H_2N_{10}O_7$ (302.12): C 15.90, H 0.67, N 46.36; found: C 15.93, H 0.75, N 45.68.

Bis(hydrazinium) 3,3′-dinitramino-4,4′-bifurazane (7): 3,3′-Dinitramino-4,4′-bifurazane (500 mg, 1.94 mmol) was suspended in a few milliliters of methanol and hydrazine hydrate (194 mg, 3.88 mmol) was added to the yellowish solution. The mixture was heated until boiling and the hot solution was filtered. After cooling down to room temperature Hy_2DNABF precipitated yielding 580 mg (1.80 mmol, 93%) of slightly orange crystals. DSC (5 °C min^{-1},°C): 230 °C (dec.); BAM: drop hammer: 6 J (< 100 μm); friction tester: 120 N (< 100 μm); ESD: 0.3 J (< 100 μm); IR (ATR): $\tilde{\nu}$ = 3311 (m), 3228 (m), 3192 (m), 3192 (m), 3053 (m), 2992 (m), 2861 (m), 2704 (m), 2611 (m), 2506 (w), 2280 (w), 2106 (w), 1954 (w), 1838 (w), 1747 (w), 1666 (w), 1619 (m), 1578 (m), 1531 (m), 1508 (s), 1439 (s), 1389 (s), 1278 (s), 1179 (s), 1115 (s), 1087 (s), 1014 (s), 977 (vs), 916 (s), 866 (s), 813 (s), 770 (s), 734 (s), 724 cm^{-1} (s); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3235 (2), 1594 (51), 1506 (100), 1418 (61), 1287 (5), 1046 (30), 1015 (72), 982 (9), 934 (4), 879 (9), 839 (16), 768 (2), 743 (5), 596 (5), 572 (15), 507 (9), 491 (4), 372 (3), 302 (9), 243 (16), 212 (5), 141 (16), 113 (25), 93 (48), 79 cm^{-1} (20); ^{1}H NMR (270 MHz, [D$_6$]DMSO, 25 °C,): δ = 6.89 ppm (s, 5H, $N_2H_5^+$); ^{13}C{^{1}H} NMR (270 MHz, [D$_6$]DMSO, 25 °C,): δ = 158.6 (C–NNO_2), 142.3 ppm (–ON=C–C=NO–); *m/z* (FAB$^+$): 33.1 [$N_2H_5^+$]; *m/z* (FAB$^-$): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_4H_{10}N_{12}O_6$ (322.20): C 14.91, H 3.13, N 52.17; found: C 15.43, H 3.10, N 52.09.

Bis(hydroxylammonium) 3,3′-dinitramino-4,4′-bifurazane (8): 50% hydroxylamine (1.32 g, 20 mmol) in methanol (20 mL) was added to 3,3′-dinitramino-4,4′-bifurazane (2.58 g, 10 mmol) dissolved in methanol (30 mL). The precipitate was filtered and dried in air yielding 3.14 g (9.69 mmol, 97%) of **8** as a colorless solid. DSC (5 °C min^{-1},°C): 141 °C (dec.); BAM: drop hammer: 11 J (< 100 μm); friction tester: 288 N (< 100 μm); ESD: 0.1 J (< 100 μm); IR (ATR): $\tilde{\nu}$ = 3143 (w), 2923 (w), 2715 (w), 1738 (w), 1604 (w), 1584 (w), 1514 (m), 1446 (s), 1380 (m), 1276 (s), 1217 (m), 1190 (m), 1106 (w), 1014 (m), 985 (w), 928 (m), 880 (w), 825 (vs), 769 (m), 724 (w), 693 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3113 (11), 1607 (55), 1506 (100), 1420 (92), 1396 (12), 1293 (7), 1050 (24), 1016 (63), 887 (12), 842 (18), 578 (12), 505 cm^{-1} (9); ^{1}H NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 9.98 (s, H, NH_3OH^+); ^{13}C{^{1}H} NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 158.7 ppm (C–NNO_2), 142.2 (–ON=C–C=NO–); *m/z* (FAB$^+$): 34.1 [NH_4O^+]; *m/z* (FAB$^-$): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_4H_8N_{10}O_8$ (324.17): C 14.82, H 2.49, N 43.21; found: C 15.16, H 2.59, N 41.99.

Bis(ammonium) 3,3′-dinitramino-4,4′-bifurazane (9a/9b): Ammonia (25%, 1.5 mL) in methanol (20 mL) was added to 3,3′-dinitramino-4,4′-bifurazane (2.58 g, 10 mmol) dissolved in methanol (20 mL). The precipitate was filtered and dried in air yielding 2.77 g (9.48 mmol, 95%) of **9a** as a colorless solid. Crystals of **9b** were obtained from water. DSC (5 °C min^{-1}): 230 °C (dec.); BAM: drop hammer: 10 J (< 100 μm); friction tester: 324 N (< 100 μm); ESD: 0.2 J (< 100 μm); IR (ATR): $\tilde{\nu}$ = 3027 (w), 1739 (w), 1512 (m), 1441 (s), 1372 (m), 1282 (s), 1010 (w), 983 (m), 914 (m), 870 (w), 819 (vs), 773 (m), 735 (w), 721 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 1595 (71), 1509 (80), 1503 (100), 1417 (60), 1285 (4), 1049 (41), 1010 (56), 876 (8), 835 (14), 745 (6), 593 (4), 572 (10), 506 cm^{-1} (7); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 7.12 ppm (s, 4H, NH_4^+); ^{13}C{^{1}H} NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 158.7 (C–NNO_2), 142.3 ppm (–ON=C-C=NO–); *m/z* (FAB$^+$): 18.1 [NH_4^+]; *m/z* (FAB$^-$): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_4H_8N_{10}O_6$ (292.17): C 16.44, H 2.67, N 47.94; found: C 16.50, H 2.78, N 46.91.

Bis(triaminoguanidinium) 3,3′-dinitramino-4,4′-bifurazane (10): 3,3′-Dinitramino-4,4′-bifurazane (500 mg, 1.94 mmol) was suspended in a few milliliters of water and triaminoguanidine (412 mg, 3.88 mmol) was added to the yellowish solution. The mixture was heated until everything dissolved. After cooling down to room temperature TAG_2DNABF precipitated in a yield of 751 mg (1.61 mmol, 83%) as a beige solid. DSC (5 °C min^{-1},°C): 203 °C (dec.); BAM: drop hammer: 3 J (< 100 μm); friction tester: 360 N (< 100 μm); IR (ATR): $\tilde{\nu}$ = 3563 (w), 3460 (w), 3337 (m), 3271 (m), 2285 (w), 1688 (s), 1590 (m), 1507 (s), 1443 (s), 1405 (s), 1361 (s), 1324 (s), 1282 (vs), 1224 (m), 1187 (m), 1129 (s), 1106 (m), 1053 (w), 1001 (s), 980 (s), 914 (s), 860 (m), 802 (s), 770 (s), 734 (m), 724 (m), 676 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3343 (6), 3244 (4), 1647 (4), 1595 (53), 1501 (100), 1420 (47), 1399 (42), 1356 (5), 1281 (7), 1138 (6), 1046 (39), 1008 (94), 930 (5), 888 (15), 872 (20), 821 (9), 767 (5), 743 (7), 642 (3), 590 (5), 567 (25), 503 (9), 476 (3), 417 (7), 371 (7), 291 (16), 242 (18), 92 cm^{-1}(58); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 8.56 (s, 3H, $C(NH)_3$), 4.32 ppm (s, 6H, $C(-NH_2)_3$); ^{13}C{^{1}H} NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 159.4 ($C(NHNH_2)_3$), 158.8 (C–NNO_2), 142.3 ppm (–ON=C–C=NO–); *m/z* (FAB$^+$): 105.1 [$CH_9N_6^+$]; *m/z* (FAB$^-$): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_6H_{18}N_{20}O_6$ (466.34): C 15.45, H 3.89, N 60.07; found: C 16.23, H 3.72, N 59.31.

Bis(guanidinium) 3,3′-dinitramino-4,4′-bifurazane (11): 3,3′-Dinitramino-4,4′-bifurazane (500 mg, 1.94 mmol) was suspended in a few milliliters of water, and dissolved guanidinium carbonate (350 mg, 1.94 mmol) was added to the clear solution and heated until everything dissolved. After cooling down to room temperature, small crystalline needles precipitated to give 580 mg (1.54 mmol, 79%). DSC (5 °C min^{-1},°C): 280 °C (dec.); BAM: drop hammer: 40 J (100–500 μm); friction tester: 360 N (100–500 μm).IR (ATR): $\tilde{\nu}$ = 3448 (s), 3346 (m), 3267 (m), 3196 (m), 2773 (w), 2293 (w), 1742 (w), 1647 (s), 1567 (m), 1510 (s), 1443 (s), 1394 (s), 1362 (m), 1332 (m), 1275 (vs), 1157 (s), 1105 (m), 1063 (m), 1009 (m), 983

(s), 920 (s), 862 (s), 806 (s), 773 (s), 733 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1602 (47), 1565 (5), 1549 (5), 1498 (100), 1419 (61), 1387 (25), 1282 (4), 1050 (33), 1017 (52), 1009 (55), 936 (3), 874 (9), 820 (13), 744 (7), 570 (12), 533 (7), 501 (9), 372 (6), 296 (12), 251 cm^{-1} (16); ^{1}H NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 6.92 (s, $C(NH_2)_3$), 3.39 ppm (s, 2H; H_2O); $^{13}C\{^1H\}$ NMR (270 MHz, [D$_6$]DMSO, 25 °C) δ = 158.8 (C–NNO_2), 158.4 ($C(NH_2)_3$), 142.3 ppm (–ON=C–C=NO–); *m/z* (FAB^+): 60.1 [$CH_6N_3^+$]; *m/z* (FAB^-): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_6H_{12}N_{14}O_6$ (376.25): C 19.15, H 3.21, N 52.12; found: C 19.43, H 3.09, N 51.84.

Bis(aminoguanidinium) 3,3′-dinitramino-4,4′-bifurazane (12): 3,3′-Dinitramino-4,4′-bifurazane (500 mg, 1.94 mmol) was suspended in a few milliliters of water. After two equivalents of aminoguanidinium bicarbonate (528 mg, 3.88 mmol) were added, the mixture was heated until boiling and the hot solution was filtered. The solvent was removed in vacuum and the residue was suspended and recrystallized from water to yield 561 mg (1.38 mmol, 71 %) of **12**. DSC (5 °C min^{-1},°C): 210 °C (m.p.), 215 °C (dec.); BAM: drop hammer: 10 J (100–500 μm); friction tester: 360 N (100–500 μm); IR (ATR): $\tilde{\nu}$ = 3470 (m), 3329 (m), 3185 (m), 2721 (w), 2293 (w), 1754 (w), 1680 (s), 1658 (s), 1648 (s), 1586 (m), 1510 (s), 1441 (s), 1398 (s), 1336 (s), 1279 (vs), 1217 (w), 1191 (w), 1102 (w), 1081 (m), 1014 (w), 982 (m), 917 (m), 867 (s), 815 (s), 771 (s), 739 (m), 716 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3333 (5), 3275 (4),1599 (59), 1535 (3), 1501 (100), 1419 (43), 1389 (15), 1284 (4), 1225 (2), 1047 (24), 1015 (47), 969 (8), 881 (10), 835 (18), 767 (3), 746 (4), 591 (2), 570 (11), 510 (8), 372 (4), 296 (6), 253 cm^{-1} (8); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 8.53 (s, 1H, $CNHNH_2$), 7.20 (s, 2H, CNH_2), 6.67 (s, 2H, CNH_2), 4.65 (s, 2H, NNH_2), 3.33 ppm (s, 2H; H_2O); $^{13}C\{^1H\}$ NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 159.3 ($C(NH_2)_2NHNH_2$), 158.8 (C–NNO_2), 142.3 ppm (–ON=C–C=NO–); *m/z* (FAB^+): 75.1 [$CH_7N_4^+$]; *m/z* (FAB^-): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_6H_{14}N_{16}O_6$ (406.28): C 17.74, H 3.47, N 55.16; found: C 17.99, H 3.32, N 54.88.

Bis(diaminouronium) 3,3′-dinitramino-4,4′-bifurazane (14b): 3,3′-Dinitramino-4,4′-bifurazane (500 mg, 1.94 mmol) was suspended in a few milliliters of methanol and 2 equiv of diaminourea (350 mg, 3.88 mmol) were added. The mixture was heated until everything dissolved. After cooling down to room temperature **14b** crystallized as colorless needles. Yield: 812 mg (1.85 mmol, 96 %). DSC (5 °C min^{-1},°C): 192 °C (dec.); BAM: drop hammer: 40 J (< 100 μm); friction tester: 360 N (< 100 μm); IR (ATR): $\tilde{\nu}$ = 3369 (w), 3232 (m), 2988 (w), 2882 (w), 2695 (w), 1674 (m), 1620 (m), 1594 (m), 1559 (w), 1512 (s), 1443 (m), 1410 (s), 1364 (w), 1336 (m), 1264 (vs), 1168 (s), 1119 (w), 979 (w), 951 (m), 910 (s), 866 (m), 809 (s), 780 (m), 762 (m), 739 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C,): $\tilde{\nu}$ = 3370 (2), 3251 (6), 2981 (2), 2703 (2), 1649 (2), 1595 (70), 1560 (6), 1503 (100), 1419 (83), 1399 (13), 1385 (9), 1315 (4), 1285 (6), 1180 (6), 1123 (3), 1044 (44), 1008 (78), 930 (12), 873 (12), 829 (25), 747 (12), 589 (9), 562 (7), 499 (13), 477 (3), 371 (8), 304 (16), 247 (32), 161 (30), 135 (48), 103 (43), 91 (74), 83 cm^{-1} (86); ^{1}H NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 7.78 ppm (br s, $C(NHNH_2)_2$); $^{13}C\{^1H\}$ NMR (270 MHz, [D$_6$]DMSO, 25 °C): δ = 159.6 ($C(NHNH_2)_2$), 158.8 (C–NNO_2), 142.3 ppm (–ON=C–C=NO–); *m/z* (FAB^-): 257.1 [$C_4HN_8O_6^-$]; elemental analysis calcd (%) for $C_6H_{14}N_{16}O_8$ (438.28): C 16.44, H 3.22, N 51.13; found: C 16.76, H 3.04, N 50.67.

Bis(hydroxylammonium) 3,3′-dinitramino-4,4′-azofurazane (23): Dinitraminoazofurazane (1.43 g, 5 mmol) was dissolved in methanol (20 mL) and a solution of hydroxylamine (0.66 g, 50 %) in methanol (20 mL) was added. The solvent was evaporated in vacuo and ether (10 mL) were added to the solid which was filtered yielding 1.41 g (80 %) of **23a** as an orange solid. The dihydrate **23b** crystallized from water. Crystals of **23a** were obtained from methanol/ether. DSC (5 °C min^{-1},°C): 150 °C (dec.); BAM: drop hammer: 4 J (100–500 μm); friction tester: 130 N; ESD: 0.13 J (100–500 μm); IR (ATR): $\tilde{\nu}$ = 2930 (m), 2712 (w), 1738 (m), 1605 (w), 1582 (w), 1540 (m), 1456 (m), 1417 (w), 1388 (m), 1285 (vs), 1263 (s), 1228 (s), 1160 (m), 1052 (m), 1007 (m), 950 (m), 887 (w), 811 (m), 773 (w), 744 (w) 698 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 1553 (3), 1498 (17), 1476 (18), 1433 (100), 1258 (9), 1233 (16), 1021 (10), 921 (5), 874 (4), 809 (3), 496 cm^{-1} (3); $^{13}C\{^1H\}$ NMR (270 MHz, [D$_6$]DMSO, 25 °C,): δ = 160.4 (C-N=N-C), 153.1 ppm (C–NNO_2); *m/z* (FAB^+): 34.1 [NH_4O^+]; *m/z* (FAB^-): 285.0 [$C_4HN_{10}O_6^-$]; elemental analysis calcd (%) for $C_4H_8N_{12}O_8$ (352.18): C 13.64, H 2.29, N 47.73; found: C 13.18, H 2.57, N 45.45.

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Synthesis and Characterization of Diaminobisfuroxane

Dennis Fischer,[a] Thomas M. Klapötke,*[a] and Jörg Stierstorfer[a]

Dedicated to Dr. Vladimir Golubev on the occasion of his 65th birthday

Keywords: Energetic materials / Nitrogen heterocycles / Oxygen heterocycles / Density functional calculations / Isomerization

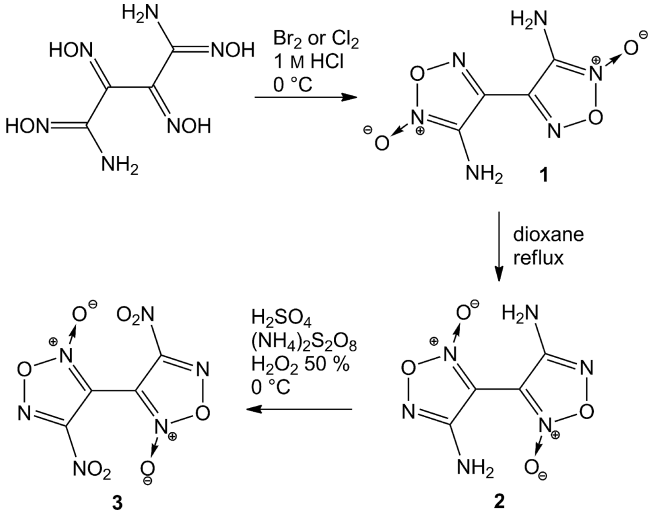
The synthesis of 3,3′-diamino-4,4′-bisfuroxane and its isomer 4,4′-diamino-3,3′-bisfuroxane was explored for the first time. In addition, the structure of highly dense (2.007 g cm^{-3} at 100 K) and energetic 4,4′-dinitro-3,3′-bisfuroxane was determined. The energetic properties of the compounds, including their thermal behavior and sensitivities, were determined, and their heat of formation and explosive properties were calculated.

Introduction

Among the class of oxadiazoles,[1] 1,2,5-oxadiazole-2-oxides (furoxanes) have especially reached great attendance in energetic materials chemistry, as they combine high nitrogen and oxygen contents often with high densities.[2] Density, oxygen balance, and heat of formation are important performance parameters for energetic materials. Superior densities can mostly be achieved when two heterocycles are linked by their carbon atoms, which has impressively be demonstrated on 5,5′-bistetrazoles[3] and 3,3′-bis-1,2,4-triazoles.[4] Aminofuroxanes have been described in the literature, although diaminofuroxane has never been isolated.[5]

Results and Discussion

3,3′-Diamino-4,4′-bisfuroxane (**1**) was synthesized from tetraoximodiaminobutane[6] by oxidation with bromine or chlorine at 0 °C in dilute hydrochloric acid (Scheme 1). The tetraoxime was dissolved and **1** precipitated immediately upon the slow addition of the halogen. Rearrangement toward the thermodynamically more stable 4,4′-diamino-3,3′-bisfuroxane (**2**) was achieved by heating **1** in dioxane. The yield was about 40%, but no attempt was made to improve the reaction conditions or those of the next step. The mixed isomer was not observed. The oxidation of **2** was attempted under various conditions. Lastly, only oxidation with peroxodisulfuric acid yielded a small amount of 4,4′-dinitro-3,3′-bisfuroxane (**3**). In that reaction, **2** was suspended in a mixture of concentrated H_2SO_4 and 50% H_2O_2, and $(NH_4)_2S_2O_8$ was then added. The mixture was stirred at a temperature of 30 °C and later at 50 °C. After quenching on ice, extracting with dichloromethane, drying with $MgSO_4$, and removing the solvent, a few crystals of 4,4′-dinitro-3,3′-bisfuroxane (**3**) were obtained from the yellowish mass in low yield. Every attempt to oxidize **1** to the corresponding nitrofuroxane by using these or similar conditions was not successful.



Scheme 1. Synthesis of **1**–**3**.

The structures of compounds **1**–**3** were determined by low-temperature X-ray diffraction (for details see the Supporting Information). Crystals suitable for XRD were obtained from water (for **1** and **2**) and dichloromethane (for **3**). All three compounds crystallize in common space

[a] Department of Chemistry, Ludwig Maximilians University of Munich,
Butenandtstrasse 5–13, 81377 Munich, Germany
E-mail: tmk@cup.uni-muenchen.de
http://www.chemie.uni-muenchen.de/ac/klapoetke/

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groups, that is $P2_1/c$ for **1**, *Pbcn* for **2**, and $P2_1/n$ for **3**. The molecular moieties are shown in Figures 1–3.

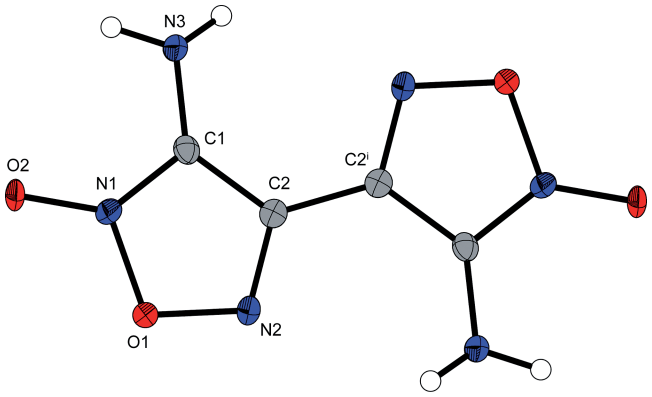

Figure 1. Molecular structure of **1** with the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level, and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry code: (i) 2 – *x*, –*y*, –*z*.

The densities of the amino derivatives are high relative to those of other aminofuroxanes (e.g., 4-amino-3-methylfuroxane:[7] 1.51 g cm^{-3} at r.t.) and are in a similar range (1.893 g cm^{-3} for **1** and 1.848 g cm^{-3} for **2**, both at 173 K). In the structure of **1**, the furoxane rings as well as the amine nitrogen atoms are planar. Also, the amine groups are almost planar but H3A is twisted out of the plane by 25.4°. The structure forms a network of hydrogen bonds between the amine groups and O2 of two adjacent molecules.

In contrast, the planar aminofuroxane rings in **2** are twisted by 48°. The amine groups are almost planar but H3A is again twisted out of the plane by 30.8°. The structure again forms a network of hydrogen bonds between the amine groups and O2 atoms. In addition, hydrogen bonding consists of intramolecular hydrogen bonds, as indicated in Figure 2.

Compound **3** (Figure 3) crystallizes with a remarkably high density of 2.007 g cm^{-3} at 100 K, although no hydrogen bonds can be formed. The unit cell contains four molecules. The furoxane rings are twisted by 126° towards each other. The nitro group containing N3 is twisted out of the adjacent ring plane by 4°. The other nitro group is twisted by 12°.

In the ^{1}H NMR spectra, the amine protons of **1** and **2** can be observed as broad singlets at δ = 5.6 and 6.6 ppm, respectively. Because of their symmetric nature, the ^{13}C NMR spectra reveal two singlets at δ = 141.8 and 122.5 ppm for **1** and at δ = 157.1 and 98.8 ppm for **2**. The high-field shifted signals belong to C3 of the furoxane rings.

The differential scanning calorimetry (DSC) curves of **1** and **2** are shown in Figure 4; they were acquired by using a heating rate of 5 °C min^{-1}. Compound **1** started to decompose at 160 °C, whereas **2** was found to be slightly more stable (170 °C). The enthalpy of formation (Table 1) of **1** is 424 kJ mol^{-1}, whereas the heat of formation of **2** is slightly lower at 359 kJ mol^{-1}. This indicates that **1** is the kinetically favored product and **2** is the thermodynamically favored product. Therefore, **2** could be obtained from **1** by simple

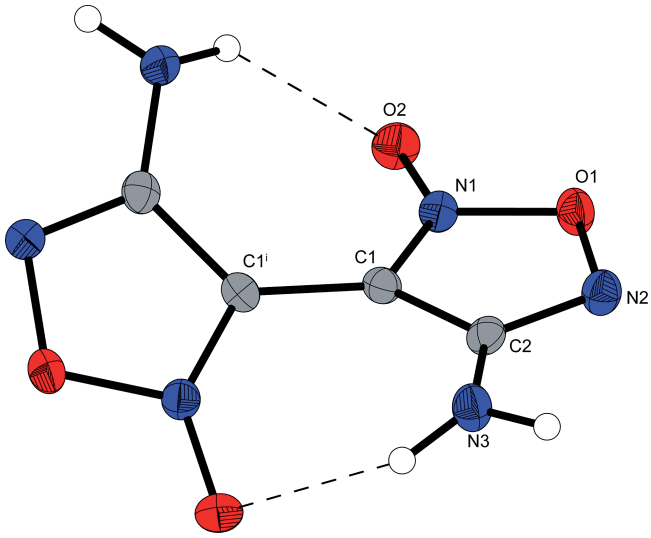

Figure 2. Molecular structure of **2** with the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level, and hydrogen atoms are shown as small spheres of arbitrary radius. Symmetry code: –*x*, *y*, 0.5–*z*.

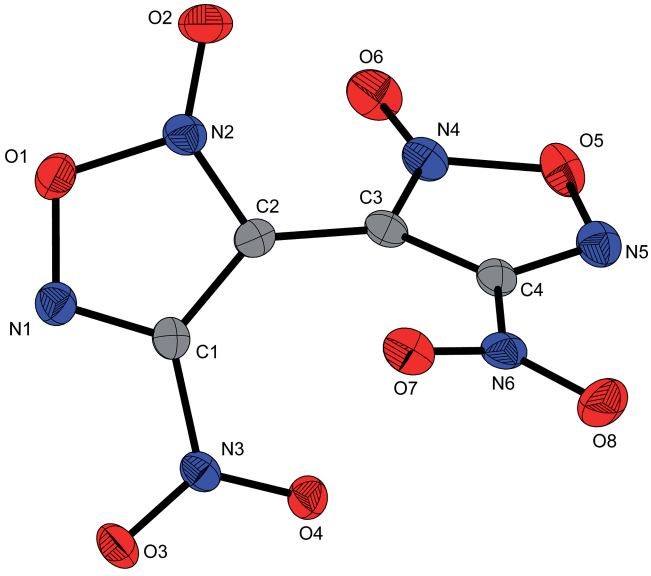

Figure 3. Molecular structure of **3** with the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level, and hydrogen atoms are shown as small spheres of arbitrary radius.

heating. The same trend was obtained by calculation of the enthalpies of formation of **3** (449 kJ mol^{-1}) and the fictive nitro sister compound (479 kJ mol^{-1}) of **1**.

Compound **2** is also less sensitive than **1** to impact; it showed a value of 10 J compared to 6 J for **1**. This trend in impact sensitivities is in accordance with the theory of Pollitzer and Murray.[8] In that theory, the calculated electrostatic potentials (ESP) of the surfaces of the molecules can be related to the impact sensitivities. In contrast to nonenergetic organic molecules for which the positive potential is larger but weaker in strength, in energetic compounds usually more extensive regions with larger and stronger positive potentials are observed; this can be related to increased im-

Table 1. Energetic properties of **1**–**3** compared to those of RDX.

	1	**2**	**3**	RDX
Formula	$C_4H_4N_6O_4$	$C_4H_4N_6O_4$	$C_4N_6O_8$	$C_3H_6N_6O_6$
FW [g mol^{-1}]	200.11	200.11	260.08	222.12
IS [J][a]	6	10	–	7.5 [9]
FS [N][b]	> 360	> 360	–	120
ESD [J][c]	0.5	0.6	–	0.2
N [%][d]	42.00	42.00	32.31	37.84
Ω_{CO_2} [%][e]	–47.97	–47.97	0	–21.61
$T_{dec.}$ [°C][f]	160	170	140 (est.)	205
ρ [g cm^{-3}][g]	1.893 (173 K)	1.848 (173 K)	2.007 (173 K)	1.858 (90 K)[10]
	1.858 (298 K)	1.814 (298 K)	1.970 (298 K)	1.806 (298 K)[11]
$\Delta_f H_m$° [kJ mol^{-1}][h]	423.8	358.7	448.9	86
$\Delta_f U$° [kJ kg^{-1}][i]	2204.2	1879.0	1792	489
EXPLO5 6.02 values:				
$-\Delta_{ex} U$° [kJ kg^{-1}][j]	6193	5878	7740	5908
T_{det} [K][k]	4010	3891	5452	3852
P_{CJ} [kbar][l]	354	326	412	347
$V_{det.}$ [m s^{-1}][m]	9007	8740	9525	8855
V° [L kg^{-1}][n]	710	718	677	785

[a] Impact sensitivity according to the BAM drophammer (method 1 of 6). [b] Friction sensitivity according to the BAM friction tester (method 1 of 6). [c] Electrostatic discharge sensitivity (OZM ESD tester). [d] Nitrogen content. [e] Oxygen balance. [f] Temperature of decomposition according to DSC (onset temperatures at a heating of 5 °C min^{-1}). [g] Low-temperature X-ray densities were converted into room-temperature values by the volume expansion formula $\rho_{298\,K} = \rho_T/[1 + \alpha_v(298–T_0)]$; $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}. [h] Heat of formation. [i] Energy of formation. [j] Heat of detonation. [k] Temperature of detonation. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of gases after detonation.

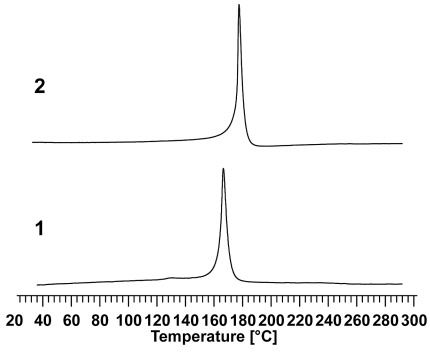

Figure 4. DSC plots (*exo* up) of compounds **1**–**3** at a heating rate of 5 °C min^{-1}.

pact sensitivities. In Figure 5, it can be clearly seen that the positive ESP region of **1** (more sensitive) is larger and also stronger than that of **2**.

The calculated detonation properties of **1** are in the range of commonly used cyclotrimethylenetrinitramine (RDX), and those of **2** are slightly below. The high heat of formation of **3** with a good oxygen balance and a high density yields a remarkably high detonation pressure of 412 kbar. However, owing to the lack of low molecular weight detonation products (no hydrogen content) the detonation velocity is "only" calculated to be 9525 m s^{-1}. The energy of explosion of **3** (7740 kJ kg^{-1}) was calculated to be outstandingly high. DSC and sensitivities of **3** were not determined because of the small amount of material obtained and the poor reproducibility of the oxidation reaction.

Conclusions

3,3′-Diamino-4,4′-bisfuroxane and 4,4′-diamino-3,3′-bisfuroxane were synthesized for the first time. The com-

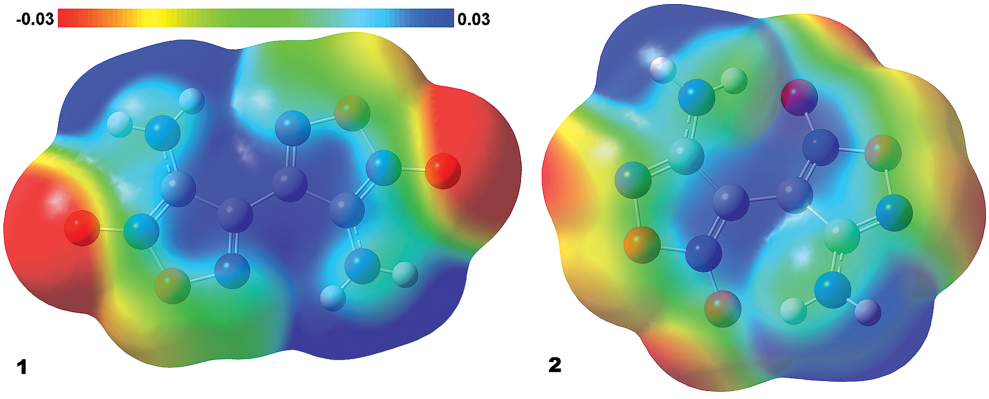

Figure 5. Depiction of the calculated [B3LYP/6-31G(d,p)] electrostatic potentials of **1** and **2**. The 3D isosurface of electron density is shown between –0.03 hartree (electron-rich regions) and +0.03 hartree (electron-poor regions).

pounds were verified by using NMR, IR, and Raman spectroscopy, mass spectrometry, differential scanning calorimetry, and single-crystal X-ray diffraction. The energetic properties of these compounds were calculated by using the computer code EXPLO5 6.02, and the sensitivities were determined by using BAM standard methods. The compounds show similar energetic properties, similar to commonly used RDX, but their temperature stability was found to be slightly lower. Additionally, the X-ray structure of 4,4′-dinitro-3,3′-bisfuroxane was obtained after oxidation of aminobifuroxane with peroxysulfuric acid. So far, the reaction conditions could not be improved to obtain acceptable yields and a pure product. 4,4′-Dinitro-3,3′-bisfuroxane shows a remarkably high density of 2.007 g cm^{-3}. Excellent detonation parameters were also calculated for this compound. To date, no experimental evidence for the existence of the isomer 3,3′-dinitro-4,4′-bisfuroxane (predicted to be also highly energetic) could be obtained.

Experimental Section

General Methods: All reagents and solvents were used as received (Sigma–Aldrich, Fluka). Tetraoximodiaminobutane was prepared according to a literature procedure.[6] Decomposition points were measured with a Linseis PT10 DSC by using a heating rate of 5 °C min^{-1} and were checked with a Büchi Melting Point B-450 apparatus. Infrared spectra were recorded by using a Perkin–Elmer Spektrum One FTIR instrument. Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. The impact and friction sensitivity data were explored by using a BAM drophammer and a BAM friction tester, and electrostatic sensitivity was determined by using an electric spark tester ESD 2010EN (OZM Research).

3,3′-Diamino-4,4′-bisfuroxane (1): Diaminotetraoximobutane (787 mg) was dissolved in the smallest amount of 1 M HCl possible. Br_2 (1.233 g) was added dropwise at 0 °C over 45 min. After stirring for another 45 min at 0 °C, precipitated **1** was filtered and dried in air, yield 602 mg (78%). DSC (5 °C min^{-1}): 160 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3388 (w), 3273 (w), 3175 (w), 1653 (vs), 1599 (s), 1491 (s), 1432 (s), 1322 (w), 1049 (s), 957 (s), 892 (m), 717 (m) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3261 (17), 3154 (8), 1681 (13), 1618 (2), 1595 (100), 1469 (97), 1382 (10), 1260 (14), 1025 (10), 895 (11), 761 (8), 709 (18), 521 (4), 356 (34), 344 (18), 249 (3) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 3.5–6.8 ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 141.8, 122.5 ppm. MS (DEI+): *m/z* = 200.1 [M]$^+$. $C_4H_4N_6O_4$ (200.11): calcd. C 24.01, H 2.01, N 42.00; found C 23.78, H 2.06, N 40.34. BAM drophammer: 6 J. Friction tester: >360 N. ESD: 0.5 J.

4,4′-Diamino-3,3′-bisfuroxane (2): Compound **1** (1000 mg) was suspended in dioxane (30 mL). The suspension was heated at reflux for 4 h, the solvent was removed, and cold water (30 mL) was added. Compound **2** (410 mg, 41%) was isolated by filtration. DSC (5 °C min^{-1}): 170 °C (dec.). IR (ATR): $\tilde{\nu}$ = 3441 (m), 3347 (m), 1617 (s), 1607 (s), 1571 (vs), 1546 (w), 1527 (s), 1438 (s), 1200 (m), 1192 (m), 923 (s), 845 (m), 737 (m) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3349 (40), 1628 (73), 1554 (17), 1520 (60), 1458 (7), 1443 (3), 1387 (77), 1291 (4), 1221 (4), 1189 (22), 1113 (3), 1004 (11), 862 (3), 788 (11), 713 (3), 692 (2), 664 (49), 637 (3), 586 (19), 562 (10), 456 (6), 377 (2) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 6.65 ppm. ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 157.1, 98.8 ppm. MS (DEI+): *m/z* = 200.1 [M]$^+$. $C_4H_4N_6O_4$ (200.11): calcd. C 24.01, H 2.01, N 42.00; found C 24.95, H 2.06, N 40.63; BAM drophammer: 10 J. Friction tester: >360 N. ESD: 0.6 J.

Oxidation of 2: Compound **2** (1000 mg) was dissolved in conc. H_2SO_4 (5 g). This solution was dropped into a suspension of $(NH_4)_2S_2O_8$ (14 g) in 50% H_2O_2 (28 g) while keeping the temperature below 30 °C. The suspension was stirred at 30 °C for 4 h and then stirred at 50 °C for another 1 h. The solution was poured onto crushed ice (50 g) and extracted with dichloromethane (4 × 25 mL). After drying with magnesium sulfate, the organic phase was left to crystallize. In the yellow liquid there were a few single crystals of **3** suitable for X-ray diffraction.

CCDC-1025977 (for **1**), -1025976 (for **2**), and -1025978 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Further information about the calculations and the X-ray data.

Acknowledgments

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Potassium 1,1′-Dinitramino-5,5′-bistetrazolate: A Primary Explosive with Fast Detonation and High Initiation Power**

Dennis Fischer, Thomas M. Klapötke, and Jörg Stierstorfer*

Abstract: *Adequate primary explosives such as lead azide mostly contain toxic ingredients, which have to be replaced. A new candidate that shows high potential, potassium 1,1′-dinitramino-5,5′-bistetrazolate (K_2DNABT), was synthesized by a sophisticated synthetic procedure based on dimethylcarbonate and glyoxal. It was intensively characterized for its chemical (X-ray diffraction, EA, NMR and vibrational spectroscopy) and physico-chemical properties (sensitivity towards impact, friction, and electrostatic, DSC). The obtained primary explosive combines good thermal stability with the desired mechanical stability. Owing to its high heat of formation (326 kJ mol^{-1}) and density (2.11 g cm^{-3}), impressive values for its detonation velocity (8330 m s^{-1}) and pressure (311 kbar) were computed. Its superior calculated performance output was successfully confirmed and demonstrated by different convenient energetic test methods.*

Primary explosives are substances that show a very rapid transition from deflagration to detonation and generate a shock-wave that makes transfer of the detonation to a less sensitive secondary explosive possible.[1,2] Lead azide and lead styphnate are the most commonly used primary explosives today.[3,4] However, the long-term use of these compounds has caused considerable lead contamination in military training grounds and costly clean-up operations waste money that could better be spent improving the defense capability of our forces.[5] A recent article published on December 4, 2012 in the Washington Post entitled "Defense Dept. Standards On Lead Exposure Faulted"[6] stated: *"… it has found overwhelming evidence that 30-year-old federal standards governing lead exposure at Department of Defense firing ranges and other sites are inadequate to protect workers from ailments associated with high blood lead levels, including problems with the nervous system, kidney, heart, and reproductive system."*

The most prominent and most promising lead azide replacement today is copper(I) 5-nitrotetrazolate (DBX-1, Figure 1) which was developed by Fronabarger, Williams, et al. at PSEMC.[7–9] Despite its promise as a "greener" alternative for lead azide, DBX-1 has shown a tendency to decompose with periodate salts, thus inhibiting its explosive activity.[10] More research is needed to determine long-term storage and potential compatibility of the material with the chemicals it would come in contact with in an energetic formulation.

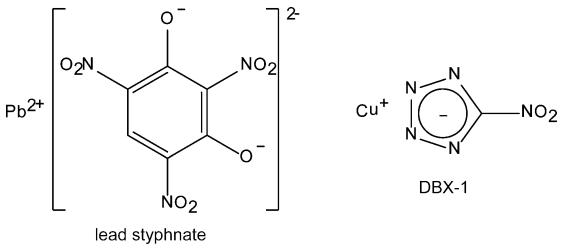

Figure 1. Structures of lead styphnate and copper(I) 5-nitrotetrazolate (DBX-1).

A "green" lead azide replacement needs to possess the following properties: a) insensitivity to light; b) sensitivity to detonation (but not too sensitive to handle and transport); c) stability to at least 180 °C; d) stability upon storage for long periods of time; e) being free of toxic metals; f) being free of toxic perchlorate; and g) ease and safety of synthesis.[3]

Herein, we report the synthesis and characterization of the new primary explosive potassium dinitraminobistetrazolate (K_2DNABT), which only contains potassium as the metal and is an alternative to lead azide. Many tetrazoles have been described as energetic materials.[11] While 5-nitriminotetrazoles are commonly known, 1-dinitramino-tetrazoles are very rare, which is due to their hard accessibility.[12] In theory, unprotected 1,1′-diamino-5,5′-bistetrazole[12] could be nitrated, but the amination of 5,5′-bistetrazole is a procedure with low yield and high effort, so an alternative route was developed. Looking for better starting materials, the bisnitrileimine seems to be a suitable precursor for this molecule. Unfortunately unprotected bisnitrilimine is only known as its diphenyl derivative,[13] so another more easily removable protecting group than a phenyl moiety was chosen. The following synthetic process describes the synthesis of K_2DNABT starting from commercially available dimethyl carbonate. The carbonate reacts with hydrazine hydrate to methyl carbazate **1**.[14] The condensation reaction with half an equivalent of glyoxal forms **2**,[15] which is subsequently oxidized with NCS (N-chlorosuccinimide) to the corresponding chloride. Substitution with sodium azide offers the diazide (in only 38% yield), which is then cyclized with hydrochloric acid in a diethyl ether suspension. The N-methoxycarbonyl-protected 1,1′-diamino-5,5′-bistetrazole (**5**) is gently nitrated with N_2O_5. An alkaline aquatic work-up with KOH precipitates dipotassium K_2DNABT (Scheme 1).

[*] D. Fischer, Prof. Dr. T. M. Klapötke, Dr. J. Stierstorfer
Ludwig Maximilian University Munich, Department of Chemistry
Butenandtstrasse 5–13, Haus D, 81377 München (Germany)
E-mail: tmk@cup.uni-muenchen.de
Homepage: http://www.hedm.cup.uni-muenchen.de

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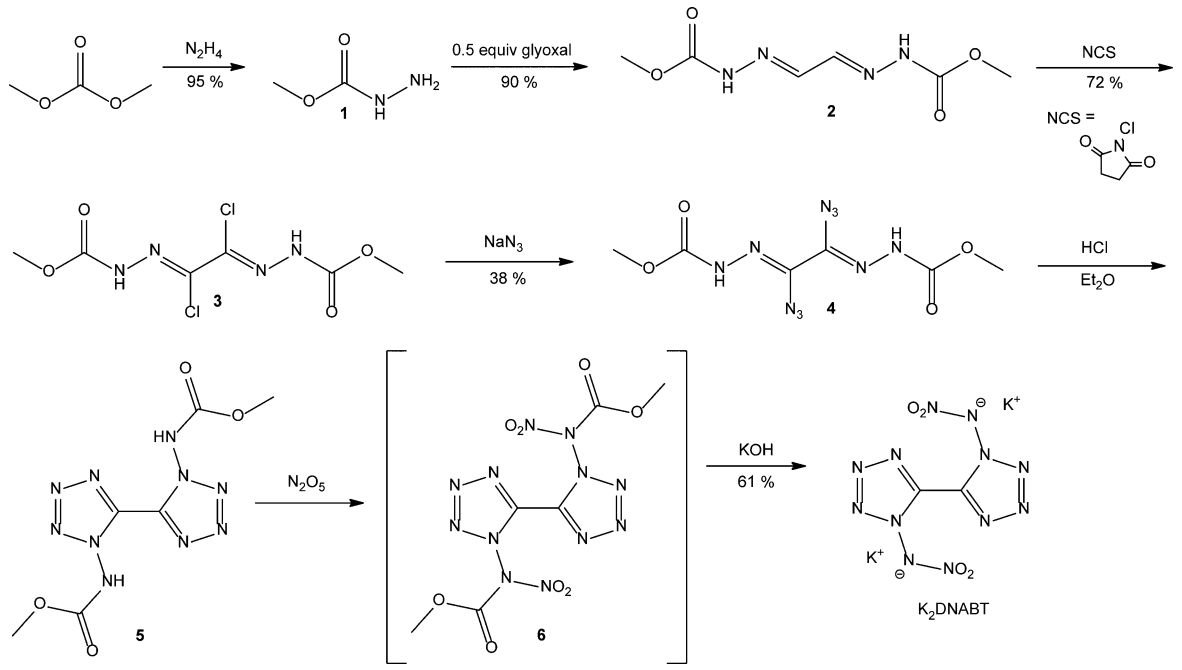

Scheme 1. Synthetic pathway towards K_2DNABT.

All of the intermediate products can be used as obtained; no column chromatography is required. Fortunately K_2DNABT shows low water solubility, which facilitates isolation and purification. The toxicity of K_2DNABT in water was determined using the known luminous bacteria method with *Vibrio fischeri* NRRL-B-11177.[16] The EC_{50} concentration of this compound after 30 min of incubation time is higher than 1.4 $g\,L^{-1}$. With a value above 1 $g\,L^{-1}$, a compound can basically be considered as nontoxic.

The molecular structure of K_2DNABT in the solid state (Figure 2) was determined by low-temperature single-crystal X-ray diffraction.[17] It crystallizes in the triclinic space group $P\bar{1}$ with a density of 2.172 $g\,cm^{-3}$ at 100 K. The potassium atoms are coordinated irregularly by either the nitrogen atoms N2, N3, N5 or the nitro oxygen atoms O1 and O2. Both tetrazole rings as well as atom N5 are almost planar to each other. The nitro groups are twisted out of this plane by almost 75°.

Several energetic tests were performed ensuring the suitability of K_2DNABT as a primary explosive. The friction and impact sensitivity is comparable to $Pb(N_3)_2$. Along with the successful ignition of one gram of RDX by 40 mg of K_2DNABT, a flame test (Figure 3d) and a "hot needle test" (see the Supporting Information for videos) indicated the instant detonation of the material in contact with a flame or a hot metal needle.

Several detonation parameters were calculated using the EXPLO5 code[19] in its latest version 6.02 using a calculated heat of formation and density (recalculated from the X-ray structure 100 K value to room temperature). It can be seen from Table 1 that K_2DNABT easily outperforms lead azide in all critical detonation parameters, while the sensitivities (impact, friction, and electrostatic discharge) are in the same range. The experimental explosive work released was

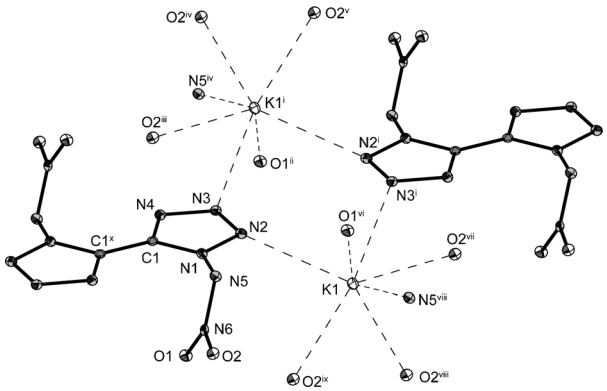

Figure 2. Molecular structure of K_2DNABT with cation coordination. Ellipsoids are set at 50% probability. Selected bond lengths [Å]: C1–C1^{i} 1.453(4), N1–C1 1.352(3), N4–C1 1.322(3), N1–N2 1.355(2), N1–N5 1.394(2), N5–N6 1.332(3), O1–N6 1.248(2), O2–N6 1.261(2); selected torsion angles [°]: C1-N1-N5-N6 75.3(3), N1-C1-C1^{i}-N4 −1.5(4), O1-N6-N5-N1 1.6(3). Symmetry codes: (i) 1−*x*, 1−*y*, 1−*z*; (ii) −*x*, 1−*y*, 1−*z*; (iii) *x*, *y*, 1+*z*; (iv) 1−*x*, −*y*, 1−*z*; 1; (v) 1+*x*, *y*, 1+*z*; (vi) 1+*x*, *y*, *z*; (vii) 1−*x*, 1−*y*, −*z*; (viii) *x*, 1+*y*, *z*; (ix) −*x*, 1−*y*, −*z*; (x) −*x*, −*y*, 1−*z*.

demonstrated by a detonation (Figure 3b) against an aluminum block in comparison with the commonly used lead azide. Owing to their good flowability, both compounds were simply poured into the steel block and ignited unpressed. The indentation is 1.4 mm, whereas lead azide reaches only 0.2 mm, using 500 mg of each compound (Figure 3c). Additionally, K_2DNABT shows excellent thermal stability. The compound was heated up to 100 °C and the temperature was held for 48 h. No loss of mass or any decomposition was observed (the TGA plot is shown in the Supporting Information). A violent decomposition was observed at 200 °C using

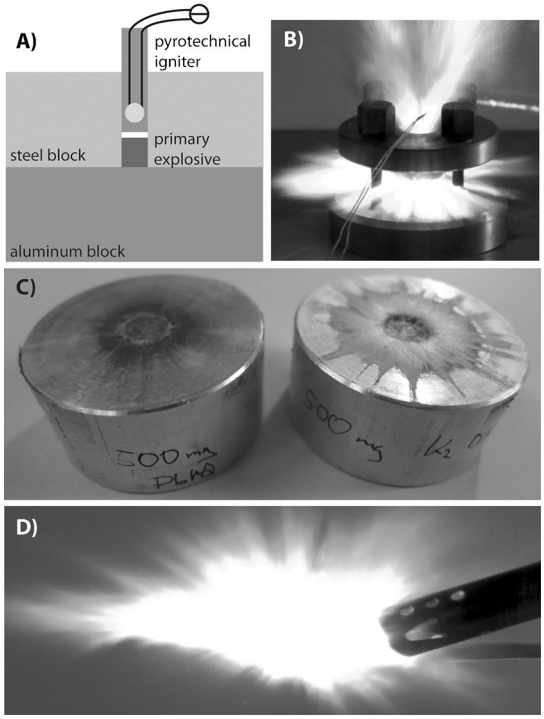

Figure 3. A) Setup of explosive work test; B) moment of detonation; C) result of explosive work test (left: $Pb(N_3)_2$, right: K2DNABT); D) flame test of K_2DNABT at the moment of detonation.

Table 1: Comparison of the energetic properties and calculated performance data of lead azide and K_2DNABT.

	$Pb(N_3)_2$	K_2DNABT
Formula	N_6Pb	$C_2K_2N_{12}O_4$
M [g mol^{-1}]	291.3	334.3
IS [J][a]	2.5–4	1
FS [N][b]	0.1–1	≤ 1
ESD [J][c]	< 0.005	0.003
N [%][d]	28.9	50.3
Ω [%][e]	−11.0	−4.8
$T_{Dec.}$ [°C][f]	ca. 315	200
ρ [g cm^{-3}][g]	4.8	2.172 (100 K) 2.11 (298 K)[18]
$\Delta_f H_m°$ [kJ mol^{-1}][h]	450.1	326.4
$\Delta_f U°$ [kJ kg^{-1}][i]	1574.9	1036.1
EXPLO5 6.02 (BKWG-S)		
$-\Delta_{Ex}U°$ [kJ kg^{-1}][j]	1569	4959
T_{det} [K][k]	3401	3424
P_{CJ} [kbar][l]	338	317
V_{det} [m s][m]	5920	8330
V_0 [L kg][n]	252	489

[a] Impact sensitivity according to the BAM drop hammer (method 1 of 6). [b] Friction sensitivity according to the BAM friction tester (method 1 of 6). [c] Electrostatic discharge sensitivity (OZM ESD tester). [d] Nitrogen content. [e] Oxygen balance. [f] Temperature of decomposition according to DSC (onset temperatures at a heating rate of 5 deg min^{-1}). [g] Density at RT. [h] Heat of formation. [i] Energy of formation. [j] Heat of detonation. [k] Temperature of detonation. [l] Detonation pressure. [m] Detonation velocity; volume of gases after detonation. [n] Gas volume after detonation.

a DSC experiment (heating rate of 5 deg min^{-1}). All tests point to the fact that this material is a suitable and non-toxic replacement for lead azide, with a straightforward synthesis from commonly available chemicals.

Experimental Section

The detailed experimental description of the whole synthetic procedure is shown in Scheme 1; the general methods are given in the Supporting Information.

Dipotassium dinitraminobistetrazolate (K_2DNABT): Compound **5** (1 g, 3.52 mmol) was suspended in 50 mL dry acetonitrile and cooled to 0–5 °C. N_2O_5 (1.5 g, 13.9 mmol) was added and the mixture was stirred at this temperature. After all of the starting material was dissolved (1–2 h), the solution was stirred for additional 30 min. Then 2 M KOH (14 mL) was added and the mixture was stirred vigorously at ice bath temperature. Additional KOH solution was added until the pH of the aqueous phase stayed constantly at 12 or above. The precipitated solid was filtered and suspended in 20 mL of ice water, stirred for 5 min, and filtered again, yielding 720 mg (61 %) of finely powdered colorless K_2DNABT.

DSC (5 °C min^{-1}): 200 °C (dec); IR (KBr): $\tilde{\nu} = 3450$ (m), 1635 (w), 1440 (s), 1382 (w), 1360 (w), 1300 (vs), 1256 (m), 1163 (w), 1124 (w), 1031 (w), 998 (w), 872 (w), 773 (w), 729 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu} = 1610$ (100), 1455 (9), 1270 (12), 1251 (19), 1142 (6), 1084 (14), 1016 (34), 992 (4), 889 (2), 750 (2), 732 (3), 512 (7), 301 cm^{-1} (4); EA ($C_2K_2N_{12}O_4$, 334.30): C 7.19, N 50.28 %; found: C 7.62, N 47.95 %; *m/z* (FAB$^-$): 257 ($C_2HN_{12}O_4^-$); BAM drop hammer: 1 J; friction tester: < 5 N; ESD: 3 mJ.

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Energetic alliance of tetrazole-1-oxides and 1,2,5-oxadiazoles†‡

Dennis Fischer, Thomas M. Klapötke,* Marius Reymann, Jörg Stierstorfer and Maurus B. R. Völkl

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The connection of highly endothermic heterocycles with high nitrogen as well as oxygen content is a recent trend in the development of new energetic materials in order to increase densities and stabilities. Bis(1-hydroxytetrazolyl)furazane (**9**) and bis(1-hydroxytetrazolyl)furoxane (**10**) were synthesized for the first time from dicyanofurazane and dicyanofuroxane, respectively. Several nitrogen-rich compounds (*e.g.* ammonium and hydroxylammonium) and metal salts thereof were prepared. Most compounds were characterized by single crystal X-ray diffraction. In addition all compounds were analyzed by vibrational spectroscopy (IR and Raman), multinuclear NMR spectroscopy, elemental analysis and DSC measurements. The heats of formation of **4**, **5**, **15–16**, **20** and **24** were calculated using the atomization method based on CBS-4M enthalpies. With these values and the experimental (X-ray) densities several detonation parameters such as the detonation pressure, velocity, energy and temperature were computed using the EXPLO5 code (V.5.05). In addition, the sensitivities towards impact, friction and electrical discharge were tested using the BAM drop hammer and friction tester as well as a small scale electrical discharge device.

Introduction

Research towards insensitive replacements for hexogen (RDX), octogen (HMX) and nitropenta (PETN) is still of particular interest in our and many other research groups worldwide. RDX has been identified as toxic and possibly carcinogenic.[1] Several attempts to synthesize appropriate replacements for RDX have been made in the recent past using tetrazole oxides.[2–4] The purpose of this study was to combine furazanes (1,2,5-oxadiazoles) and furoxanes (1,2,5-oxadiazole-2-oxides) with tetrazole oxides. The connection of highly endothermic heterocycles with high nitrogen as well as oxygen content is a recent trend in the development of new energetic materials in order to obtain powerful materials with great density and appropriate oxygen balance on the one hand, and perfect stability on the other hand. Tetrazoles (without N-oxide) have already been attached to furazanes[5] and furoxanes.[6] The resulting literature known compounds **24** and **25** as well as the new ones **9** and **10** are displayed in Fig. 1.

Various nitrogen rich salts of **9** and **10** as well as metal salts were synthesized to investigate their properties as potential energetic ingredients. The resulting 3,4-(1-oxidotetrazolyl)-furoxanes and furazanes are capable and fairly stable compounds in their deprotonated form.

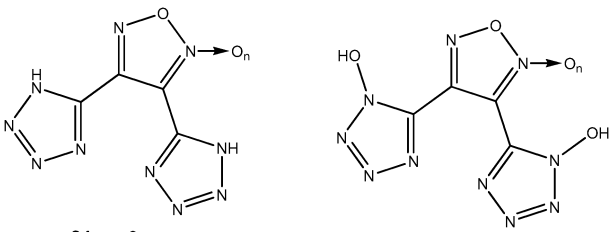


Fig. 1 Compounds **9** and **10** and the literature known compounds **24**[5] and **25**.[6]

Results and discussion

Synthesis

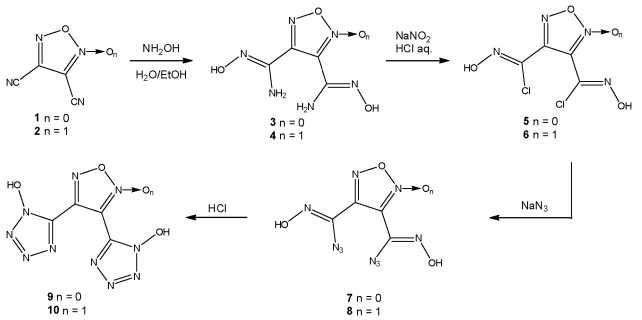
Compounds **9** and **10** were synthesised using a similar protocol from dicyanofurazane[7] and dicyanofuroxane[8] as depicted in Scheme 1.

Hydroximoylamines **3** and **4** are made from the nitriles by exothermic addition of aqueous hydroxylamine in ethanol in about 85% yield. Hydroximoyl chlorides **5** and **6** were synthesized from **3** and **4** by diazotization in 15% HCl and subsequently

Ludwig Maximilians University of Munich, Department of Chemistry, Energetic Materials Research, Butenandtstr. 5-13, D-81377 Munich, Germany. E-mail: tmk@cup.uni-muenchen.de

† Dedicated to Dr. Klaus Römer on the occasion of his 75th birthday.

‡ Electronic supplementary information (ESI) available: X-ray diffraction data, computations, and general experimental methods. CCDC 988403–988414. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4nj01351d



Scheme 1 Synthetic protocol for **9** and **10**.

extracted into diethyl ether. The reaction of **5** and **6** with sodium azide in aqueous ethanol affords hydroximoylazides **7** and **8**, respectively, which are also extracted into diethyl ether. The dried ether phase was saturated with gaseous HCl at 0 °C and stirred for 24 h in order to close the desired aromatic tetrazole-oxide rings. Compounds **9** and **10** are obtained as slightly yellow sticky oils after removal of the ethereal HCl solution.

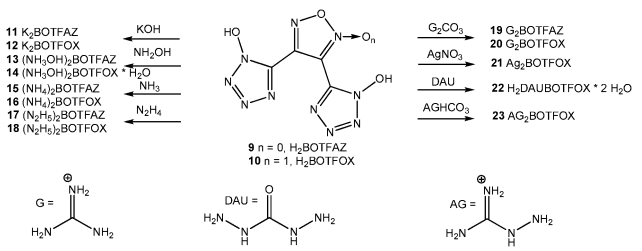
Salts of compounds **9** and **10** could be easily prepared by the addition of a base or the corresponding carbonates/bicarbonates to aqueous solutions of **9** and **10**. The silver salt of **10** precipitated upon the addition of aqueous silver nitrate. An overview of the salts prepared in this work is given in Scheme 2.

Crystal structures

Single crystals for XRD of compounds **3–6**, **11**, **12**, **14–17**, **20** and **23** could be obtained during this work. Crystallographic data and parameters as well as CCDC numbers are given in Tables S1 and S2 in the ESI.‡

In general, all bond lengths and angles were observed as expected and are comparable to similar crystal structures of furazanes,[9] furoxanes,[10] and tetrazole-oxides[11] in the literature. Compound **3** crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell. The molecular unit is generated by C_2 symmetry through atom O1 and bond C1–C1^{i}. The density (1.667 g cm^{-3} at 100 K) of **3** is significantly smaller than that of the corresponding furazane **7** (1.780 g cm^{-3} at 173 K). Compound **4** crystallizes in the monoclinic space group $P2_1/n$. The molecular moieties are depicted in Fig. 2.

Hydroximoyl chlorides **5** and **6** crystallize in the monoclinic ($P2_1/n$) and orthorhombic ($P2_12_12_1$) crystal systems with four molecules in the unit cell. The molecular units are shown in Fig. 3. The density of furazane (1.909 g cm^{-3} at 100 K) again is slightly lower than that of furoxane (1.949 g cm^{-3} at 100 K).



Scheme 2 Synthesis of salts **11–23**.

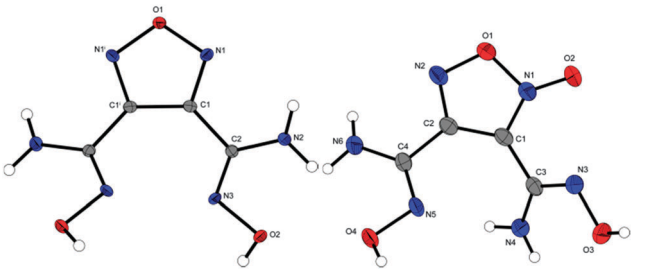


Fig. 2 Molecular moieties of **3** and **4** thermal ellipsoids are drawn at the 50% probability level. **3**: Symmetry code: 1 − x, y, 1.5 − z. Selected bond lengths (Å): O2–N3 1.4194(18), N3–C2 1.291(2), N2–C2 1.351(2); **4**: Selected bond lengths (Å): O2–N1 1.224(2), N4–C3 1.354(3), N4–C3 1.354(3), O3–N3 1.418(3).

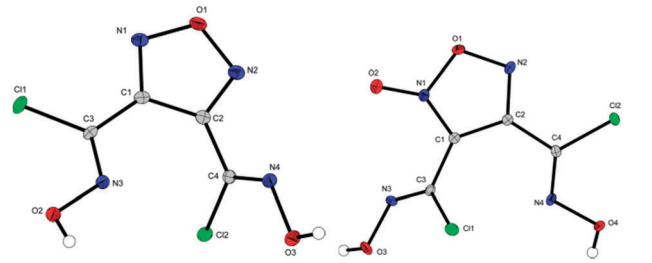


Fig. 3 Molecular moiety of **5** and **6**. Thermal ellipsoids are drawn at the 50% probability level.

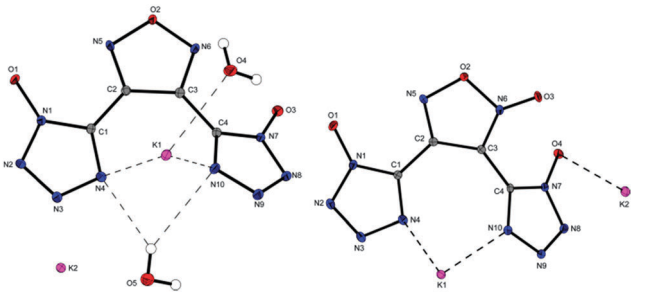


Fig. 4 Molecular moiety of **11** and **12**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths of **11**/**12** (Å): O1 N1 1.297(2), N1 N2 1.340(2), N1 C1 1.360(2), N2 N3 1.321(2), N3 N4 1.344(2) O2 N5 1.3822(19), O2 N6 1.430(2), O3 N6 1.2343(19)

Crystal structures of both potassium salts were obtained. The structure of furazane **11**, which crystallizes in the monoclinic space group $P2_1/c$, contains two crystal water molecules resulting in a lower density of 1.926 g cm^{-3} (at 100 K). For furoxane **12** (triclinic, $P\bar{1}$) a density of 2.156 g cm^{-3} at 100 K has been calculated. In both structures two rings (containing atoms C1 and C2/C3) are almost in plane while the third one is significantly deviated. Molecular moieties of **11** and **12** are depicted in Fig. 4.

Compound **14**·H_2O could only be obtained in the crystalline form with inclusion of one crystal water molecule (Fig. 5).

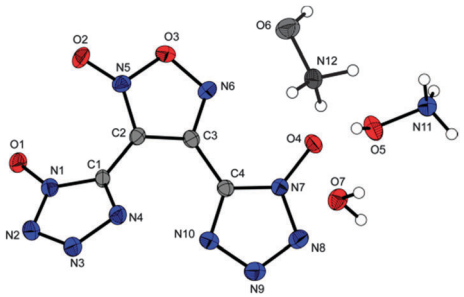


Fig. 5 Molecular moiety of **14**·H_2O. Thermal ellipsoids are drawn at the 50% probability level.

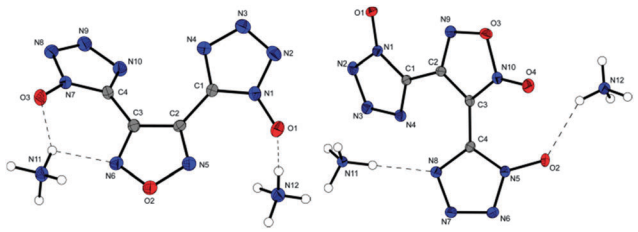


Fig. 6 Molecular moiety of ammonium salts **15** and **16**. Thermal ellipsoids are drawn at the 50% probability level. **15**: Selected bond lengths (Å): C1–C2 1.455(3), C2–C3 1.432(3), C3–C4 1.457(3), O1–N1 1.327(2), O3–N7 1.327(2); **16**: Selected bond lengths (Å): C1–C2 1.450(3), C3–C2 1.423(3), C3–C4 1.449(3), O1–N1 1.3187(19), O2–N5 1.323(2), O4–N10 1.231(2).

It crystallizes in the monoclinic space group $P2_1$ with a density of 1.794 g cm^{-3} at 173 K.

Bisammonium salt **15** crystallizes in the orthorhombic space group *Pbca* with a calculated density of 1.686 g cm^{-3} at 298 K. The corresponding bisammonium furoxane salt **16** crystallizes with a higher density of 1.748 g cm^{-3} (at 293 K) in the monoclinic space group $P2_1/c$. Both structures shown in Fig. 6 are dominated by strong hydrogen bonds involving all NH_4^+ protons.

The products of deprotonation of **9** with hydrazine and different guanidinium bases have not been obtained as single crystals. The hydrazinium salt of **9** crystallizes in the triclinic ($P\bar{1}$) crystal system and with a density of 1.727 g cm^{-3} at 236 K without inclusion of crystal water. The molecular moiety is shown in Fig. 7.

The bisguanidinium salt **20** (Fig. 8) crystallizes in the monoclinic space group $C2/c$ and with a density of 1.739 g cm^{-3} at 100 K (Fig. 8).

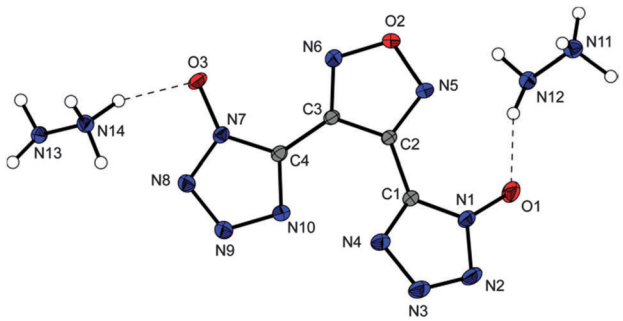


Fig. 7 Molecular moiety of hydrazinium salt **17**. Thermal ellipsoids are drawn at the 50% probability level.

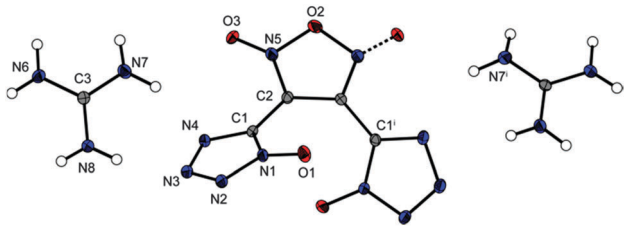


Fig. 8 Molecular moiety of guanidinium salt **20**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry code: (i) $1 - x, y, 0.5 - z$.

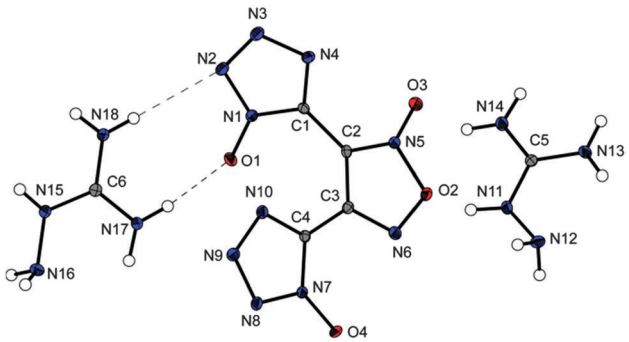


Fig. 9 Molecular moiety of aminoguanidinium salt **23**. Thermal ellipsoids are drawn at the 50% probability level.

In contrast to **20**, the aminoguanidinium salt **23** shows a slightly lower crystal density of 1.692 g cm^{-3}. The asymmetric unit of the monoclinic ($P2_1/c$) cell is shown in Fig. 9.

NMR spectroscopy

All ^{1}H NMR and ^{13}C NMR shifts of compounds **1–23** are gathered in Table 1. The ^{1}H NMR spectra of **9** and **10** exhibit both a broad singlet at around 7 ppm although **10** has no

Table 1 ^{1}H NMR and ^{13}C NMR shifts of all compounds

C	^{1}H NMR shift [ppm]	^{13}C NMR shift [ppm]
1	—	136.3, 106.7
2	—	134.7, 106.8, 105.0, 99.5
3	10.33, 6.20	148.7, 142.1
4	10.64, 10.08, 6.98, 6.08	151.6, 142.5, 139.8, 109.9
5	13.61	148.7, 122.9
6	13.78, 13.58	150.6, 124.8, 120.3, 110.2
7	12.85	147.1, 132.6
8	13.00, 12.75	149.4, 133.7, 130.4, 107.7
9	9.02	142.1, 136.6
10	6.67	143.4, 136.8, 134.4, 103.4
11	—	145.0, 132.8
12	—	147.7, 133.2, 130.3, 106.5
13	10.22	144.2, 133.9
14	10.27	146.4, 134.3, 131.5, 105.6
15	7.18	144.8, 133.1
16	7.22	147.2, 133.5, 130.7, 106.1
17	7.09	144.8, 133.1
18	7.16	147.1, 133.7, 130.9, 106.1
19	6.63	158.1, 144.2, 132.9
20	6.99	158.5, 146.9, 133.8, 130.9, 105.9
21	—	146.2, 133.2, 130.4, 105.4
22	6.36	158.4, 145.6, 135.1, 132.5, 105.0
23	8.70, 7.26, 6.90, 4.51	159.4, 147.0, 133.8, 130.9, 106.0

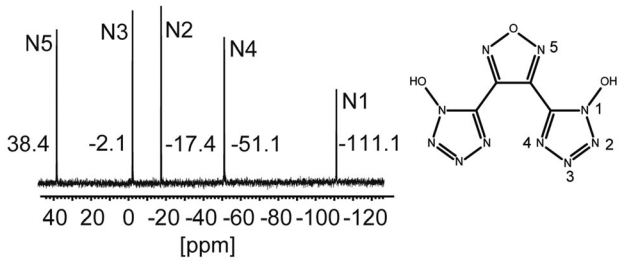


Fig. 10 $^{15}N\{^{1}H\}$ NMR spectrum of **9**.

C_{2V} symmetry anymore. The oximes in compounds **3–8** are observed in low field regions from 10.33 to 13.00 ppm. In the case of the oxime and amide protons splitting of the signals of the furoxane compounds can be observed because of the lower symmetry. In the ^{13}C NMR spectrum **9** exhibits two resonances at 142.1 ppm caused by furazane and 136.6 ppm caused by 1-hydroxytetrazole. **10** shows four resonances in the ^{13}C NMR spectra because of the lower symmetry at 136.8 and 134.4 ppm for the tetrazole oxides and at 143.4 and 103.4 ppm for the furoxane ring. Upon deprotonation the furazane signal of **9** is shifted towards lower fields up to 148.7 ppm and the tetrazole-oxide signal is shifted towards higher fields down to 132.8 ppm. The same trend was observed for **10**. Deprotonation led to a shift towards lower fields up to 149.4 and 107.7 ppm for furoxane but to a shift towards higher fields down to 133.2 and 130.3 ppm for the tetrazole-oxide resonances. The ^{15}N NMR spectrum of **9** is depicted in Fig. 10. The chemical shifts are assigned to the particular nitrogen atoms.

The carbon signals of the salts **11–23** are shifted to lower fields in comparison with their acids. No irregularities in the ^{1}H NMR and ^{13}C NMR shifts of the nitrogen-rich cations were observed.

Energetic properties

Thermal behavior (DSC). The thermal behaviour of the most important salts (with respect to their energetic behavior) of **9** and **10** is depicted in Fig. 11. The highest thermal stabilities of bis(1-oxidotetrazolyl)furaz(ox)anes are reached by the potassium salts at 277 °C (**11**) and 265 °C (**12**), respectively.

Heats of formation, sensitivities and detonation parameters. Gas phase heats of formation ($\Delta_f H^\circ_{(g,M,298)}$) were calculated theoretically using the atomization eqn (1) and CBS-4M electronic enthalpies. Details of the computations and the conversion of gas phase values into solid state values are given in the ESI.‡

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma \Delta_f H^\circ_{(atoms,298)} \quad (1)$$

Sensitivities were measured using a BAM drop hammer, a BAM friction tester[12] and a OZM electrostatic discharge device[13] (see also the Experimental part, General methods).

Detonation parameters were calculated using the computer code EXPLO5.05[14] using X-ray densities which were converted to room temperature values according to eqn (2). A coefficient of volume expansion[15] α_v of 1.5×10^{-4} K^{-1} was used. The structures of **15** and **16** were already measured at room temperature. Further explanations are gathered in the ESI.‡

$$\rho_{298K} = \rho_T/(1 + \alpha_v(298 - T_0)) \quad (2)$$

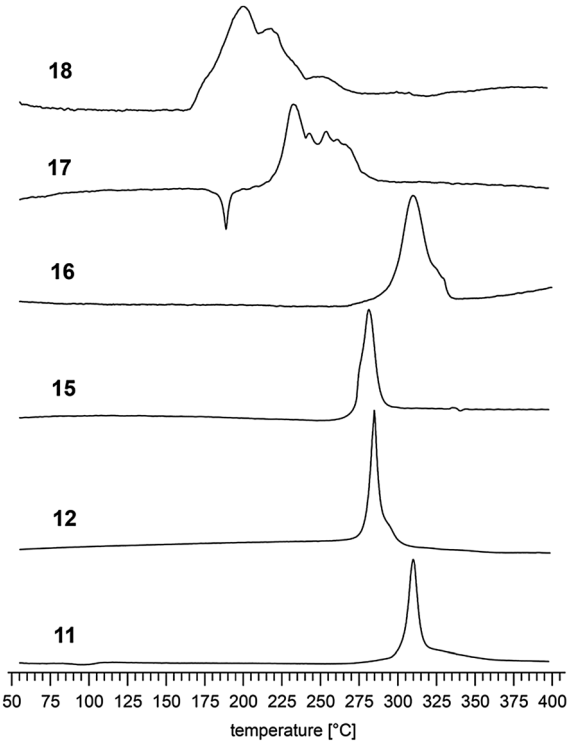


Fig. 11 DSC plots of compounds **11**, **12**, **15**, **16**, **17** and **18** at 5 °C min^{-1}.

Only the physicochemical properties of compounds **4**, **5**, **15–16**, **20** and **23** are discussed since (i) they consist only of CHNO atoms and (ii) anhydrous crystal structures were obtained. The energetic parameters in comparison with RDX (cyclotrimethylene-trinitramine) are summarized in Table 2. All compounds investigated show improved sensitivities to RDX (IS 7.4 J, FS 120 N). Especially **20** is classified as insensitive towards impact and friction. The highest heat of formation was calculated for hydrazinium salt **17** ($\Delta_f H^\circ_{(s)}$ = 947.5 kJ mol^{-1}). For energetic materials it is more convenient to look for mass based enthalpies or energies. Also the highest mass based energy of formation value ($\Delta_f U^\circ$ 3245.4 kJ kg^{-1}) was calculated for **17**. The most important detonation parameters (heat of detonation, detonation temperature, pressure, velocity of detonation, and volume of detonation gases) were calculated with the EXPLO5.05 code and are summarized in Table 2. Based on these computations, compound **17** (8843 m s^{-1}) has higher velocity of detonation than RDX (8763 m s^{-1}). However, with respect to the synthetic expenditures and the assessment of all important energetic properties (sensitivities, stabilities and performance) probably none of the compounds will be used as an explosive filler by itself.

Table 2 Energetic properties of **3**, **4**, **15–17**, **20** and **23**

	3	**4**	**15**	**16**	**17**	**20**	**23**	RDX
Formula	$C_4H_6N_6O_3$	$C_4H_6N_6O_4$	$C_4H_8N_{12}O_3$	$C_4H_8N_{12}O_4$	$C_4H_{10}N_{14}O_3$	$C_6H_{12}N_{16}O_4$	$C_6H_{14}N_{18}O_4$	$C_3H_6N_6O_6$
FW/g mol^{-1}	186.13	202.13	272.18	288.18	302.21	372.26	402.29	222.12
IS/J[a]	>40	10	9	10	7	30	8	7.4[16]
FS/N[b]	>360	240	>360	240	>360	>360	>360	120[16]
ESD/J[c]	>1.5	0.25	1.5	1	1.5	n.d.	n.d.	0.2
N/%[d]	45.15	41.58	61.75	58.32	64.89	60.20	62.67	37.84
Ω_{CO_2}/%[e]	−68.76	−55.40	−52.90	−44.41	−52.94	−60.17	−59.65	−21.61
$T_{Dec.}$/°C[f]	198	180	259	234	211	197	165	205
ρ/g cm^{-3} [g]	1.668(100 K)	1.781(173 K)			1.727(236 K)	1.739(100 K)	1.692(100 K)	1.858(90 K)[17]
	1.64(298 K)	1.75(298 K)	1.686(293 K)	1.748(293 K)	1.71(298 K)	1.69(298 K)	1.64(298 K)	1.806(298 K)[18]
$\Delta_f H_m°$/kJ mol^{-1} [h]	150.2	159.3	625.6	621.7	947.5	638.3	885.4	66.6[16]
$\Delta_f U°$/kJ kg^{-1} [i]	907.1	886.4	2402.8	2260.2	3245.4	1820.8	2311.2	400.2[16]
EXPLO5.05:								
$-\Delta_{Ex}U°$/kJ kg^{-1} [j]	4713	5323	5122	5530	5779	4532	4884	6110
T_{det}/K[k]	3286	3631	3582	3841	3813	3193	3340	4224
P_{CJ}/kbar[l]	229	287	279	313	318	261	261	351
$V_{Det.}$/m s^{-1} [m]	7727	8312	8364	8671	8843	8161	8224	8763
V_o/L kg^{-1} [n]	720	719	769	772	793	764	782	739

[a] Impact sensitivity (BAM drophammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance ($\Omega = (xO - 2yC - 1/2zH)M/1600$). [f] Start of decomposition temperature from DSC (β = 5 °C). [g] From X-ray diffraction, values for 298 K were calculated with $\rho_{298K} = \rho_T/(1 + \alpha_v(298 - T))$,[15] $\alpha_v = 1.5 \times 10^{-4}$ K^{-1}. [h] Calculated enthalpy of formation. [i] Calculated energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of detonation gases (assuming only gaseous products).

Conclusions

From this combined experimental and theoretical study the following conclusions can be drawn.

– The combination of furazanes or furoxanes with tetrazole-1-oxides is a suitable strategy in order to generate new triheterocyclic high-performing energetic materials due to their large positive heats of formation and appropriate densities.

– Generally the investigated furoxanes show mostly higher densities but lower thermal stabilities than the corresponding furazanes. Therefore, furazanes mostly are the better choice as energetic backbone heterocycles.

– The thermal stability of the tetrazole oxide anions attached to a furoxane or furazane ring is sufficient to reach decomposition temperatures above 200 °C.

Experimental part

For general methods, please see the ESI.‡

Syntheses

Bisaminohydroximoylfurazane (3). 10.8 g (90 mmol) of **1** was dissolved in 45 mL of ethanol and added within 15 min to 22.2 g (336 mmol) of 50% hydroxylamine solution, which was diluted with 90 mL of ethanol. The solvent was removed under reduced pressure until crystallization started. Upon filtering 9.3 g (50 mmol, 55%) of **3** were obtained as a yellowish powder. DSC (5 °C min^{-1}): 193 (mp.), 198 °C (dec.). Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3162 (6), 1651 (71), 1592 (17), 1535 (35), 1513 (100), 1374 (43), 1282 (6), 1126 (6), 1040 (16), 984 (32), 956 (9), 923 (8), 826 (4), 761 (6), 488 (14) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.33, 6.20 ppm. ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C), δ: 148.7, 142.1 ppm.

Bisaminohydroximoylfuroxane (4). 1.4 g of dicyanofuroxane (10 mmol) was dissolved in 30 mL of ethanol and 1.3 g of 50% hydroxylamine solution in 10 mL of ethanol was added. After stirring for 30 min the solvent was removed and the residue was suspended in 20 mL of diethyl ether. The solid was filtered yielding 1.7 g (8.4 mmol, 84%) of the yellowish product. DSC (5 °C min^{-1}): 180 (dec.)°C. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3463 (w), 3371 (w), 3309 (w), 1668 (m), 1647 (s), 1579 (s), 1539 (w), 1504 (m), 1418 (m), 1360 (m), 1311 (m), 1229 (w), 1082 (w), 1021 (w), 951 (s), 929 (s), 858 (w), 810 (m), 744 (vs), 688 (s) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3372 (12), 1671 (39), 1651 (34), 1582 (13), 1542 (100), 1507 (12), 1421 (20), 1310 (14), 1232 (14), 1107 (10), 1066 (10), 1021 (10), 956 (9), 933 (11), 860 (6), 756 (10), 639 (6), 480 (24), 370 (5), 330 (11), 299 (5), 263 (6) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.64, 10.08, 6.98, 6.08 ppm. ^{13}C{^{1}H} NMR (270 MHz, DMSO-d_6, 25 °C), δ: 151.6, 142.5, 139.8, 109.9 ppm. EA ($C_4H_6N_6O_4$, 202.13 g mol^{-1}) calc. (found): C 23.77 (23.99), H 2.99 (2.86), N 41.58 (41.45)%. IS: 10 J (<100 μm). FS: 240 N. ESD: 0.25 J.

Bischlorohydroximoylfurazane (5). 6.9 g (37 mmol) of **3** was dissolved in 200 mL of semi-conc. hydrochloric acid. A solution of 6.3 g (92 mmol) of sodium nitrite in 30 mL of water was added dropwise within one hour while maintaining the temperature below 0 °C. The solution was stirred for one hour, allowed to come to ambient temperature, diluted with 200 mL of water and was extracted with 4 × 35 mL of diethyl ether. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure to obtain 7.97 g (35 mmol, 96%) of **5** as an oily liquid which partially started to crystallize.

DSC (5 °C min^{-1}): 115 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3502 (m), 3388 (m), 2991 (w), 2877 (w), 1731 (w), 1607 (m), 1561 (w), 1507 (w), 1499 (w), 1397 (m), 1390 (m), 1376 (m), 1359 (m),

1343 (m), 1265 (m), 1193 (w), 1094 (vw), 1057 (s), 1032 (s), 999 (s), 962 (s), 900 (s), 887 (vs), 863 (s), 818 (m), 795 (w), 749 (vw), 664 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3397 (6), 2944 (9), 2245 (3), 1626 (9), 1611 (100), 1563 (14), 1509 (89), 1396 (16), 1374 (3), 1361 (2), 1273 (3), 160 (8), 1002 (3), 968 (4), 889 (18), 864 (2), 666 (29), 655 (6), 616 (5), 601 (7), 499 (7), 430 (13), 413 (3), 366 (4), 325 (7), 296 (9), 241 (19), 226 (10), 182 (8), 151 (10), 102 (55), 76 (11), 67 (6) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.61 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 148.7, 122.9 ppm. EA ($C_4H_2N_4O_3Cl_2$, 224.99 g mol^{-1}) calc. (found): C 21.35 (23.19), H 0.90 (1.53), N 24.90 (22.76)%.

Bischlorohydroximoylfuroxane (6). **4** (34.8 g, 0.2 mol) was dissolved in 500 mL of 34% hydrochloric acid (595 g, 6.0 mol). The solution was cooled with a salt-ice bath and additionally 500 g of ice was added to the solution. Sodium nitrite (31.1 g, 0.5 mol) was dissolved in little water and added dropwise over 1 h while keeping the temperature below 0 °C. Afterwards the solution was allowed to warm to ambient temperature and diluted by addition of 1 L of ice water. The product was extracted three-times with 200 mL of diethyl ether and dried over magnesium sulfate. **6** was obtained as a slightly yellow oily liquid which partially started to crystallize to give a total yield of 41.1 g (170 mmol, 81%). ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.78, 13.58 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 150.6, 124.8, 120.3, 110.2 ppm.

Bisazidohydroximoylfurazane (7). 7.96 g (35 mmol) of **5** was dissolved in 50 mL of ethanol and 6.53 g (100 mmol) of sodium azide in 50 mL water was added at 0–5 °C. The suspension was stirred for 1 h on ice, diluted with 100 mL of water and brought to pH 2 using 2 M hydrochloric acid. The product was extracted with 5 × 30 mL of diethyl ether. The organic phase was dried over magnesium sulfate. The product does not need to be isolated for the continuing steps. If the solvent is removed a yellowish oil is obtained in approx. 80% yield which partially starts to crystallize on standing. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3258 (m), 3035 (w), 2981 (w), 2855 (w), 2361 (vw), 2325 (vw), 2132 (s), 1733 (w), 1614 (m), 1558 (vw), 1516 (w), 1445 (w), 1389 (m), 1340 (s), 1272 (s), 1223 (m), 1108 (vw), 1093 (w), 1026 (s), 976 (vs), 936 (s), 899 (m), 855 (s), 819 (w), 781 (vw), 753 (w), 668 (vw) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 12.85 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.1, 132.6 ppm.

Bisazidohydroximoylfuroxane (8). **6** (3.9 g, 16 mmol) was dissolved in 20 mL of ethanol and cooled with an ice bath while an aqueous solution of sodium azide (2.6 g, 40 mmol) was added in small portions. After the addition of sodium azide, the mixture was stirred for 1 h. The yellowish solution was diluted with 70 mL of ice water, adjusted to pH 1 by addition of concentrated hydrochloric acid and extracted with 3 × 30 mL and 1 × 10 mL of diethyl ether. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. **8** was obtained as a yellowish oil in approx. 80% yield. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 13.00, 12.75 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 149.4, 133.7, 130.4, 107.7 ppm.

Bis(1-hydroxytetrazolyl)furazane (9). The ethereal solution of **7** was saturated with gaseous HCl below 5 °C, the reaction flask was sealed and was then allowed to come to ambient temperature and stirred overnight. The solvent was removed under reduced pressure and bis(1-hydroxytetrazolyl)furazane was obtained as a yellowish oily liquid. DSC (5 °C min^{-1}): 91 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3404 (w), 2255 (w), 2128 (w), 1713 (w), 1660 (m), 1463 (m), 1344 (m), 1246 (m), 1197 (m), 1103 (m), 1053 (s), 1022 (s), 1005 (s), 982 (s), 922 (s), 895 (s), 819 (vs), 758 (s), 729 (s), 709 (m), 686 (m), 673 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2982 (8), 2940 (70), 2878 (14), 1618 (100), 1453 (10), 1387 (7), 1261 (30), 1205 (6), 1111 (5), 1011 (8), 907 (10), 764 (5), 736 (15), 711 (5), 455 (10), 92 (38) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 9.02 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 142.1, 136.6 ppm. $^{15}N\{^{1}H\}$ NMR (400 MHz, DMSO-d_6, 25 °C), δ: 38.39, −2.1, −17.4, −51.1, −111.1 ppm.

Bis(1-hydroxytetrazolyl)furoxane (10). The oily compound **8** (3.3 g, 13 mmol) was dissolved in 100 mL of diethyl ether. Gaseous HCl was passed through the reaction mixture until saturation was reached at 0–5 °C and the reaction flask was sealed. After stirring overnight at room temperature the solvent was removed and bis(1-hydroxytetrazolyl)furoxane remained as a yellowish resinous substance. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3423 (w), 2460 (w), 1607 (vs), 1461 (w), 1402 (w), 1369 (m), 1301 (m), 1259 (m), 1223 (m), 1194 (w), 1135 (w), 1091 (w), 1000 (m), 965 (s), 816 (s), 762 (w), 744 (w), 728 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2997 (2), 2990 (2), 2982 (7), 2943 (44), 1612 (100), 1463 (12), 1309 (14), 1265 (35), 1227 (31), 1201 (6), 1138 (6), 1003 (12), 820 (8), 765 (9), 747 (13), 733 (14), 700 (7), 526 (7), 453 (10), 414 (6), 388 (6), 358 (8) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.67 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 143.4, 136.8, 134.4, 103.4 ppm.

Dipotassium bis(1-oxidotetrazolyl)furazane (11). An aqueous solution of **9** was brought to pH 8 with 2 M potassium hydroxide solution. The solution was left for crystallization and the dihydrate of **11** was obtained as a crystalline solid. The anhydrous compound was obtained by pouring a hot concentrated aqueous solution of **11** into the five-fold volume of ethanol and filtering. DSC (5 °C min^{-1}): 87 °C (dehy), 277 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3552 (w), 3357 (m), 3242 (w), 1665 (w), 1635 (m), 1592 (m), 1574 (w), 1542 (w), 1471 (s), 1437 (m), 1407 (s), 1372 (m), 1362 (m), 1286 (s), 1239 (s), 1173 (w), 1118 (m), 1084 (w), 1033 (m), 1015 (w), 1000 (s), 983 (vs), 912 (s), 896 (m), 834 (w), 803 (w), 771 (m), 751 (w), 727 (w), 692 (w), 664 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1594 (26), 1575 (100), 1473 (6), 1374 (13), 1240 (11), 1176 (12), 1145 (8), 1121 (4), 1085 (3), 1017 (5), 1004 (3), 774 (5), 457 (5), 98 (13), 79 (5) cm^{-1}. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 145.0, 132.8. EA ($K_2C_4H_4N_{10}O_5$, 386.37 g mol^{-1}) calc. (found): C 12.43 (13.60), H 1.04 (1.22), N 36.25 (36.72)%. MS (FAB^+) m/z: 39.0 [K^+], (FAB^-) m/z: 237.2 [$C_4HN_{10}O_3^-$]. IS: 35 J (<100 μm), FS: >360 N. ESD: 1.5 J.

Dipotassium bis(1-oxidotetrazolyl)furoxane (12). The total amount of **10** was suspended in 50 mL of ethanol and an aqueous solution of potassium hydroxide was added until pH 7 was reached. The potassium salt started to precipitate. After

addition of 20 mL of diethyl ether more precipitate could be obtained. Filtration of the mixture and air drying led to 4.9 g (15 mmol, 94% based on step **6**) of a white powder. DSC (5 °C min^{-1}): 265 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3376 (w), 3142 (w), 3087 (w), 2841 (w), 2799 (w), 2652 (w), 2449 (w), 2357 (w), 2343 (w), 2167 (w), 2000 (w), 1799 (w), 1703 (w), 1670 (w), 1648 (w), 1609 (s), 1575 (s), 1546 (s), 1464 (m), 1450 (s), 1427 (s), 1421 (s), 1396 (s), 1370 (s), 1297(m), 1231 (vs), 1195 (w), 1167 (m), 1156 (w), 1144 (w), 1115 (w), 1095 (m), 1035 (w), 1017 (m), 988 (s), 964 (s), 879 (w), 836 (s), 792 (w), 767 (s), 754 (m), 731 (m), 711 (m), 705 (w), 693 (m), 682 (m), 654 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1616 (22), 1576 (100), 1549 (35), 1449 (11), 1403 (11), 1372 (3), 1299 (5), 1235 (24), 1195 (29), 1170 (19), 1158 (6), 1147 (6), 1098 (6), 1021 (6), 992 (18), 838 (8), 769 (16), 734 (3), 713 (3), 696 (7), 685 (3), 595 (4), 558 (5), 511 (13), 456 (13), 442 (5), 411 (5), 368 (6), 341 (3), 297 (2), 260 (4), 240 (4), 166 (34), 137 (46), 122 (24), 101 (36), 77 (27) cm^{-1}. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.7, 133.2, 130.3, 106.5. MS (FAB^+): 39.0 [K^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($K_2C_4N_{10}O_4$, 330.30 g mol^{-1}) calc. (found): C 14.55 (14.64), H 0.00 (0.00), N 42.41 (41.38)%. Found: C 14.64, H 0.00, N 41.38%. IS: 10 J (<100 μm). Friction tester: 48 N (<100 μm).

Dihydroxylammonium bis(1-oxidotetrazolyl)furazane (13). 3.2 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of ethanol. 2.2 eq. of 50% hydroxylamine solution was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then removed under reduced pressure and the precipitate was filtered off. 2.9 g (9.6 mmol, 95%) of **13** was obtained as a white crystalline powder. DSC (5 °C min^{-1}): 170 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3210 (w), 3043 (w), 2885 (w), 2663 (m), 1992 (w), 1623 (w), 1602 (w), 1497 (m), 1473 (s), 1434 (m), 1429 (m), 1404 (s), 1376 (w), 1361 (s), 1285 (s), 1245 (s), 1230 (s), 1197 (m), 1180 (m), 1126 (w), 1035 (w), 1009 (m), 1000 (s), 986 (vs), 894 (m), 878 (w), 773 (m), 748 (w), 694 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1606 (15), 1588 (100), 1477 (5), 1439 (2), 1376 (14), 1289 (2), 1249 (13), 1236 (4), 1183 (16), 1147 (8), 1128 (4), 1089 (5), 1012 (16), 903 (7), 776 (4), 750 (6), 686 (2), 556 (4), 462 (10), 46 (2), 349 (2), 309 (2), 98 (14) cm^{-1}. ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.22 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.2, 133.9 ppm. EA ($C_4H_8N_{12}O_5$, 304.18 g mol^{-1}) calc. (found): C 15.79 (16.39), H 2.65 (2.67), N 55.26 (54.23)%. IS: 7 J (<100 μm). FS: 216 N (<100 μm). ESD (<100 μm): 1 J.

Dihydroxylammonium bis(1-oxidotetrazolyl)furoxane monohydrate (14). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted with 4 × 20 mL of diethyl ether. The ether was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Hydroxylamine (661 mg of 50% solution in H_2O, 0.61 mL, 10 mmol) was added while stirring. The solution was left for crystallisation. Compound **14** crystallized to give 1.7 g (4.9 mmol, 98%) yield. DSC (5 °C min^{-1}): 135 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 2976 (m), 2709 (m), 1696 (w), 1625 (s), 1591 (s), 1559 (s), 1461 (s), 1426 (m), 1399 (m), 1376 (m), 1300 (m), 1232 (vs), 1187 (m), 1020 (m), 996 (s), 964 (s), 822 (m), 757 (m), 704 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 2986 (13), 1630 (27), 1590 (100), 1567 (29), 1495 (6), 1463 (8), 1398 (14), 1300 (8), 1235 (15), 1212 (44), 1186 (6), 1137 (10), 1102 (5), 1018 (14), 1001 (33), 833 (4), 756 (8), 707 (3), 684 (3), 506 (4), 460 (7). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 10.27 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 146.4, 134.3, 131.5, 105.6 ppm. EA ($C_4H_{10}N_{12}O_7$, 338.20 g mol^{-1}) calc. (found): C 14.21 (14.30), H 2.98 (2.90), N 49.70 (48.43)%. IS: 10 J (100–500 μm). FS: 240 N (100–500 μm).

Diammonium bis(1-oxidotetrazolyl)furazane (15). 3.1 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of water. 2.2 eq. of ammonium hydroxide was added under vigorous stirring. The solvent was then removed under reduced pressure. The crude product was recrystallized from methanol, 2.66 g (8.8 mmol, 87%) of **11** was obtained as colorless crystals. DSC (5 °C min^{-1}): 259 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3134 (w), 3000 (w), 2881 (w), 2796 (w), 1665 (w), 1604 (w), 1594 (w), 1469 (m), 1440 (s), 1405 (s), 1366 (s), 1283 (s), 1229 (vs), 1181 (w), 1133 (w), 1122 (m), 1031 (m), 1014 (w), 1003 (m), 983 (s), 905 (s), 889 (m), 765 (w), 748 (s), 731 (w), 716 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1606 (31), 1594 (100), 1482 (4), 1373 (11), 1235 (20), 1182 (16), 1136 (12), 1123 (4), 1015 (6), 1005 (3), 906 (7), 767 (4), 750 (7), 612 (3), 461 (10), 305 (2), 163 (5), 129 (6), 102 (42). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.18 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.8, 133.1 ppm. EA ($C_4H_8N_{12}O_3$, 272.19 g mol^{-1}) calc. (found): C 17.65 (17.93), H 2.96 (2.95), N 61.75 (61.00)%. IS: 9 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Diammonium bis(1-oxidotetrazolyl)furoxane (16). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted with 4 × 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. The solution was adjusted to pH 7 by addition of 2 M NH_3. The solvent was removed under reduced pressure and **16** precipitated as a colorless solid to give 1.2 g (4.2 mmol, 84%) yield. Crystals of **16** were obtained from water. DSC (5 °C min^{-1}): 230 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3166 (w), 3010 (w), 2892 (w), 2801 (w), 1622 (s), 1583 (m), 1555 (m), 1462 (s), 1426 (s), 1399 (s), 1374 (m), 1297 (m), 1228 (vs), 1181 (w), 1020 (w), 996 (m), 964 (s), 832 (s), 760 (m), 744 (w), 733 (w), 706 (w), 688 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3031 (3), 1622 (29), 1585 (100), 1556 (20), 1398 (10), 1297 (4), 1229 (14), 1207 (28), 1182 (4), 1134 (9), 1102 (4), 1025 (4), 999 (8), 832 (3), 761 (4), 711 (2), 687 (2), 553 (2), 500 (4). ^1H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.22 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.2, 133.5, 130.7, 106.1 ppm. EA ($C_4H_8N_{12}O_4$, 288.18 g mol^{-1}) calc. (found): C 16.67 (16.88), H 2.80 (2.82), N 58.32 (56.18)%. IS: 10 J (<100 μm). FS: 240 N (<100 μm). ESD (<100 μm): 1 J.

Dihydrazinium bis(1-oxidotetrazolyl)furazane (17). 3.2 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid.

The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was removed under reduced pressure. The residue was dissolved in 20 mL of ethanol and 2.2 eq. of hydrazine hydrate was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then concentrated under reduced pressure and the precipitate was filtered off. The crude product was recrystallized from methanol, 2.9 g (9.4 mmol, 94%) of **17** was obtained as yellowish crystals. DSC (5 °C min^{-1}): 175 °C (mp.), 211 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3323 (w), 3187 (w), 2839 (m), 2710 (m), 2640 (m), 1604 (m), 1537 (m), 1471 (m), 1422 (w), 1402 (s), 1374 (w), 1361 (m), 1285 (s), 1232 (m), 1222 (s), 1173 (w), 1141 (m), 1115 (s), 1093 (s), 1078 (s), 1009 (w), 999 (m), 982 (s), 962 (vs), 897 (s), 874 (m), 768 (w), 758 (m), 747 (m), 731 (w), 716 (w), 697 (w), 689 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3326 (3), 3188 (4), 1609 (57), 1587 (100), 1473 (8), 1376 (15), 1235 (16), 1174 (18), 1150 (9), 1137 (5), 1087 (7), 1004 (7), 963 (10), 901 (9), 772 (7), 749 (5), 620 (3), 464 (14), 171 (4), 141 (5), 104 (9), 92 (16). ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.09 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 144.8, 133.1 ppm. EA ($C_4H_{10}N_{14}O_3$, 302.21 g mol^{-1}) calc. (found): C 15.90 (16.36), H 3.34 (3.27), N 64.89 (64.45)%. IS: 7 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Dihydrazinium bis(1-oxidotetrazolyl)furoxane (18). 1.7 g of **12** (5.6 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Hydrazinium hydroxide (0.5 g, 0.5 mL, 10 mmol) was added to the colorless solution, the solvent was removed under reduced pressure and **18** precipitated as a colorless solid to give 1.5 g (4.8 mmol, 96%) yield. DSC (5 °C min^{-1}): 160 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3563 (w), 3461 (w), 3344 (m), 3331 (m), 3285 (m), 2833 (m), 2725 (m), 2606 (m), 2105 (m), 1613 (s), 1580 (s), 1551 (s), 1512 (s), 1455 (s), 1426 (s), 1413 (s), 1391 (s), 1371 (s), 1345 (m), 1292 (m), 1230 (s), 1108 (m), 1088 (s), 1018 (m), 984 (s), 956 (s), 942 (vs), 820 (s), 773 (m), 760 (s), 746 (m), 732 (m), 704 (m), 688 (m), 679 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1613 (19), 1583 (100), 1554 (12), 1457 (4), 1396 (9), 1295 (3), 1237 (11), 1209 (30), 1181 (7), 1152 (7), 1137 (7), 1096 (7), 1018 (4), 989 (11), 946 (4), 764 (10), 734 (3), 707 (3), 692 (3), 556 (4), 500 (7), 456 (11), 439 (5), 366 (3), 324 (6), 295 (2), 159 (14), 110 (46), 88 (45) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 7.16 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 147.1, 133.7, 130.9, 106.1 ppm. MS (FAB^+): 33.0 [$N_2H_5^+$], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_4H_{10}N_{14}O_4$, 318.21 g mol^{-1}) calc. (found): C 15.10 (15.56), H 3.17 (3.24), N 61.62 (59.96)%. IS: 5 J (<100 μm). FS: 96 N (<100 μm). ESD (<100 μm): 0.5 J.

Diguanidinium bis(1-oxidotetrazolyl)furazane (19). 3.1 g (10 mmol) of **11** was dissolved in 20 mL of 2 M hydrochloric acid. The solution was extracted with 5 × 30 mL of diethyl ether and the solvent was concentrated under reduced pressure. The residue was dissolved in 5 mL of water. 1.1 eq. of a solution of guanidinium carbonate in water was added under vigorous stirring. The solution was stirred for additional 30 min, the solvent was then removed under reduced pressure and the precipitate was filtered off. The crude product was recrystallized from methanol, 3.4 g of **19** was obtained as pale yellow crystal rods. DSC (5 °C min^{-1}): 124 (mp.), 264 (dec.) °C. IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3360 (s), 3206 (m), 3119 (s), 2813 (w), 1691 (w), 1656 (vs), 1591 (m), 1582 (m), 1469 (s), 1432 (w), 1404 (s), 1363 (m), 1291 (s), 1237 (s), 1140 (m), 1126 (m), 1040 (m), 1001 (m), 987 (s), 899 (m), 882 (m), 770 (w), 750 (w), 696 (w) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3370 (2), 3229 (9), 1597 (9), 1578 (100), 1470 (5), 1368 (19), 1243 (9), 1180 (16), 1151 (6), 1128 (4), 1099 (7), 1010 (24), 906 (5), 777 (6), 752 (2), 542 (6), 462 (10), 293 (6), 136 (2), 106 (2) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.63 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.1, 144.2, 132.9 ppm. EA ($C_6H_{12}N_{16}O_3$, 356.27 g mol^{-1}) calc. (found): C 20.23 (19.56), H 3.40 (3.63), N 62.90 (59.68)%. IS: >40 J (<100 μm). FS: >360 N (<100 μm). ESD (<100 μm): 1.5 J.

Diguanidinium bis(1-oxidotetrazolyl)furoxane (20). 1.7 g of **12** (5.1 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Guanidinium carbonate (0.9 g, 5.2 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **20** precipitated to give 1.8 g (4.8 mmol, 96%) of colorless, crystalline blocks. DSC (5 °C min^{-1}): 197 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3428 (s), 3342 (s), 3161 (s), 2793 (m), 2202 (w), 1999 (w), 1640 (vs), 1590 (s), 1553 (s), 1458 (m), 1423 (s), 1400 (m), 1335 (s), 1303 (s), 1243 (s), 1226 (s), 1180 (s), 1134 (m), 1106 (m), 1089 (m), 1026 (m), 1010 (m), 986 (s), 964 (s), 846 (w), 818 (s), 763 (s), 735 (s), 726 (s), 700 (m), 692 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3267 (2), 1623 (42), 1594 (100), 1558 (40), 1460 (22), 1434 (12), 1338 (3), 1307 (27), 1234 (9), 1210 (64), 1183 (7), 1136 (15), 1109 (8), 1092 (5), 1028 (7), 1009 (69), 989 (18), 967 (3), 823 (8), 761 (12), 729 (8), 704 (9), 592 (4), 564 (11), 529 (14), 494 (11), 448 (14), 421 (14), 368 (23), 286 (7), 230 (26), 163 (26) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.99 ppm. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.5, 146.9, 133.8, 130.9, 105.9 ppm. MS (FAB^+): 60.1 [$CH_6N_3^+$], 373.1 [M + H^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_6H_{12}N_{16}O_4$, 372.26 g mol^{-1}) calc. (found): C 19.36 (19.74), H 3.25 (3.22), N 60.20 (59.93)%. IS: 30 J (100–500 μm). FS: 360 N (100–500 μm). ESD (<100 μm): 1.5 J.

Disilver bis(1-oxidotetrazolyl)furoxane (21). 0.5 g of **11** (1.5 mmol) was dissolved in 20 mL of water and an aqueous solution of silver nitrate (0.5 g, 3.0 mmol) was added, the silver salt precipitated immediately. After stirring and heating until boiling for a short time, the colorless solid was filtered off and air dried to give 0.7 g (1.4 mmol, 90%) of Ag_2BOTFOX as a monohydrate. DSC (5 °C min^{-1}): 221 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3365 (w), 3155 (w), 1628 (s), 1584 (s), 1462 (s), 1432 (s), 1397 (s), 1372 (m), 1302 (m), 1231 (vs), 1185 (m), 1092 (w), 1027 (w), 990 (m), 967 (s), 818 (s), 765 (s), 747 (m), 726 (m), 696 (m), 677 (m) cm^{-1}. $^{13}C\{^1H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 146.2, 133.2, 130.4, 105.4 ppm. MS (DEI^+): 107.0 [Ag^+]. EA ($Ag_2C_4H_2N_{10}O_5$, 485.86 g mol^{-1}) calc. (found): C 9.89 (10.09), H 0.41 (0.41), N 28.83 (28.47)%. IS: 3 J (<100 μm). FS: 16 N (<100 μm).

Diaminouronium bis(1-oxidotetrazolyl)furoxane dihydrate (22). 1.7 g of **12** (5 mmol) was dissolved in 20 mL of 2 M

hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Diaminourea (0.9 g, 10 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **22** precipitated as a colorless solid to give 1.8 g (4.8 mmol, 96%) yield. DSC (5 °C min^{-1}): 156 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3288 (w), 2964 (m), 2683 (m), 2133 (w), 1693 (m), 1618 (s), 1575 (s), 1557 (s), 1454 (s), 1427 (m), 1396 (m), 1377 (m), 1297 (m), 1233 (vs), 1180 (m), 1106 (w), 1014 (w), 990 (m), 965 (s), 826 (s), 750 (s), 734 (m), 678 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 1618 (20), 1586 (100), 1557 (20), 1453 (2), 1400 (11), 1298 (6), 1248 (9), 1209 (33), 1180 (5), 1145 (8), 1104 (5), 1016 (6), 993 (19), 830 (7), 769 (7), 736 (3), 711 (3), 691 (3), 591 (2), 502 (8), 453 (8), 407 (3), 670 (3), 242 (6), 154 (31), 102 (47) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 6.36 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 158.4, 145.6, 135.1, 132.5, 105.0. MS (FAB^-): 253.1 [$C_4HN_{10}O_4^-$], EA ($C_5H_{12}N_{14}O_7$, 380.24 g mol^{-1}) calc. (found): C 15.79 (16.23), H 3.18 (2.99), N 51.57 (51.47)%. IS: 40 J (<100 μm). FS: 216 N (<100 μm). ESD (<100 μm): 1.5 J.

Di(aminoguanidinium) bis(1-oxidotetrazolyl)furoxane (23). 1.7 g of **11** (5 mmol) was dissolved in 20 mL of 2 M hydrochloric acid and extracted four-times with 20 mL of diethyl ether. The solvent was removed under reduced pressure and the residue was dissolved in a few milliliters of water. Aminoguanidinium bicarbonate (1.4 g, 10 mmol) was added and the solution was heated while stirring. After filtration the mixture was cooled down to ambient temperature and **23** crystallized to give 1.9 g (4.7 mmol, 94%) of colorless blocks. DSC (5 °C min^{-1}): 165 °C (dec.). IR (ATR, 25 °C), $\tilde{\nu}$ (rel. int.): 3424 (w), 3359 (m), 3303 (m), 3241 (m), 3101 (w), 1668 (vs), 1620 (s), 1585 (m), 1560 (s), 1455 (m), 1428 (m), 1400 (m), 1363 (m), 1301 (m), 1238 (s), 1227 (s), 1193 (m), 1168 (m), 1095 (m), 1077 (m), 1056 (m), 1024 (w), 1009 (w), 990 (m), 961 (s), 910 (s), 823 (s), 771 (m), 758 (s), 732 (m), 710 (m) cm^{-1}. Raman (1064 nm, 400 mW, 25 °C), $\tilde{\nu}$ (rel. int.): 3363 (6), 3263 (5), 1622 (31), 1588 (100), 1562 (30), 1456 (9), 1430 (6), 1397 (7), 1365 (5), 1303 (15), 1215 (69), 1170 (10), 1138 (14), 1107 (10), 1025 (6), 1011 (5), 992 (33), 966 (14), 824 (13), 773 (8), 752 (9), 735 (5), 711 (3), 687 (2), 624 (4), 591 (4), 557 (10), 501 (16), 460 (11), 434 (6), 405 (2), 375 (12), 342 (3), 285 (3), 260 (6), 231 (20), 155 (49), 138 (64), 127 (60), 100 (77), 89 (91) cm^{-1}. ^{1}H NMR (270 MHz, DMSO-d_6, 25 °C), δ: 8.70, 7.26, 6.90, 4.51 ppm. $^{13}C\{^{1}H\}$ NMR (270 MHz, DMSO-d_6, 25 °C), δ: 159.4, 147.0, 133.8, 130.9, 106.0 ppm. MS (FAB^+): 75.1 [$CH_7N_4^+$], 403.2 [M + H^+], (FAB^-): 253.1 [$C_4HN_{10}O_4^-$]. EA ($C_6H_{14}N_{18}O_4$, 402.29 g mol^{-1}) calc. (found): C 17.91 (18.17), H 3.51 (3.47), N 62.67 (61.54)%. IS: 8 J (<100 μm). FS: 360 N (<100 μm).

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Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL) under grant no. W911NF-09-2-0018, the Armament Research, Development and Engineering Center (ARDEC) under grant no. W911NF-12-1-0467, and the Office of Naval Research (ONR) under grant nos. ONR.N00014-10-1-0535 and ONR.N00014-12-1-0538 is gratefully acknowledged. The authors acknowledge collaborations with Dr Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr Muhamed Suceska (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) for many inspired discussions. We also thank Mr Stefan Huber for sensitivity measurements.

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Energetic Materials

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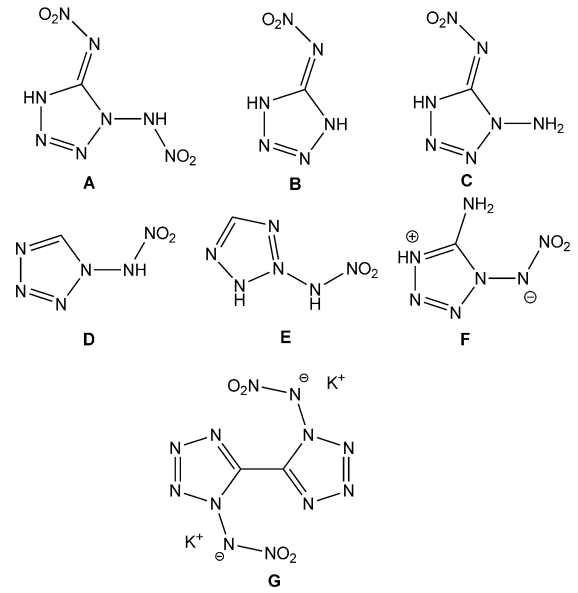
1,5-Di(nitramino)tetrazole: High Sensitivity and Superior Explosive Performance**

Dennis Fischer, Thomas M. Klapötke, and Jörg Stierstorfer*

Abstract: *Highly energetic 1,5-di(nitramino)tetrazole and its salts were synthesized. The neutral compound is very sensitive and one of the most powerful non-nuclear explosives to date. Selected nitrogen-rich and metal salts were prepared. The potassium salt can be used as a sensitizer in place of tetracene. The obtained compounds were characterized by low-temperature X-ray diffraction, IR and Raman spectroscopy, multinuclear NMR spectroscopy, elemental analysis, and DSC. Calculated energetic performances using the EXPLO5 code based on calculated (CBS-4M) heats of formation and X-ray densities support the high energetic performances of the 1,5-dinitraminotetrazolates as energetic materials. The sensitivities towards impact, friction, and electrostatic discharge were also explored.*

The 1-nitraminotetrazoles are of particular interest in the development of high-energy-density materials (HEDM) since they possess large positive heats of formation and good oxygen balances.[1] The combination of both aspects yields very powerful energetics. The known nitramino tetrazoles without alkyl chains[2] are limited to the examples shown in Scheme 1. While *C*-nitraminotetrazoles are usually synthesized by common acidic nitration conditions (for example, HNO_3; 100%), *N*-nitramino tetrazoles are synthesized by nitration of the corresponding *N*-aminotetrazoles with mild nitration reagents such as NO_2BF_4 and N_2O_5. Herein we present a new representative of this class of compounds, namely 1,5-di(nitramino)tetrazole (**1**). The synthesis of this compound has been a long-term goal in energetic materials research because of its outstanding predicted performance. To date, many attempts of direct nitration have failed.[3,4]

The synthesis of **1**, shown in Scheme 2, starts with commercially available dimethylcarbonate, which is treated with hydrazine hydrate to give the methyl carbazate (**2**). Species **2** is reacted with cyanogen azide to yield *N*-methoxycarbonyl protected 1,5-diaminotetrazole (**3**), which is then nitrated in acetonitrile with N_2O_5. The nitramide **4** is decomposed in solution with aqueous KOH to give **5** as a white precipitate from which **1** can be isolated by acidification and extraction into organic solvents.



Scheme 1. A) 1,5-di(nitramino)tetrazole (**1**) and known nitraminotetrazoles B) 5-nitraminotetrazole,[5] C) 5-nitramino-1-aminotetrazole,[6] D) 1-nitraminotetrazole,[7] E) 2-nitraminotetrazole,[7] F) 1-nitramino-5-aminotetrazole,[3] G) dipotassium 1,1′-di(nitramino)-5,5′-bitetrazolate.[8].

The ammonium (**6**), hydrazinium (**7**), and hydroxylammonium (**8**) salts are prepared by dissolving **1** in methanol and reacting it with the corresponding base in aqueous solution. In the case of **8**, an adduct of **8** with hydroxylamine (**8b**) was obtained with an excess of hydroxylamine.

Low-temperature X-ray diffraction was used to characterize all of the compounds obtained and to obtain accurate densities for performance calculations. 1,5-Di(nitramino)tetrazole (**1**) crystallizes in the orthorhombic space group $P2_12_12_1$ and a density of 1.968 g cm^{-3} at 173 K. The molecule, shown in Figure 1, is nearly planar (∡C1-N6-N5-O1 −3.9(6)°) but the *N*-nitramine is twisted out of the ring plane (∡N2-N1-N7-N8 72.0°). The proton at N4 is within the ring plane and the proton located at N7 forms pyramidal system with N8 and N1 (∡N2-N1-N7-H7 −47.9°). The bond length between N5 and N6 (1.356(2) Å) is significantly shorter than the bond length between N7 and N8 (1.462(2) Å).

The dipotassium salt of the 1,5-di(nitramino)tetrazole (**5**) crystallizes anhydrously from water in the monoclinic space group $P2_1/n$ with a density of 2.177 g cm^{-3} (173 K) and four molecules in the unit cell. Figure 2 illustrates the molecular unit of **5**. The nitramino moiety attached to the carbon is

[*] D. Fischer, Prof. Dr. T. M. Klapötke, Dr. J. Stierstorfer
Department of Chemistry, Ludwig Maximilian University
Butenandtstrasse 5–13 (D), 81377 München (Germany)
E-mail: tmk@cup.uni-muenchen.de
Homepage: http://www.hedm.cup.uni-muenchen.de

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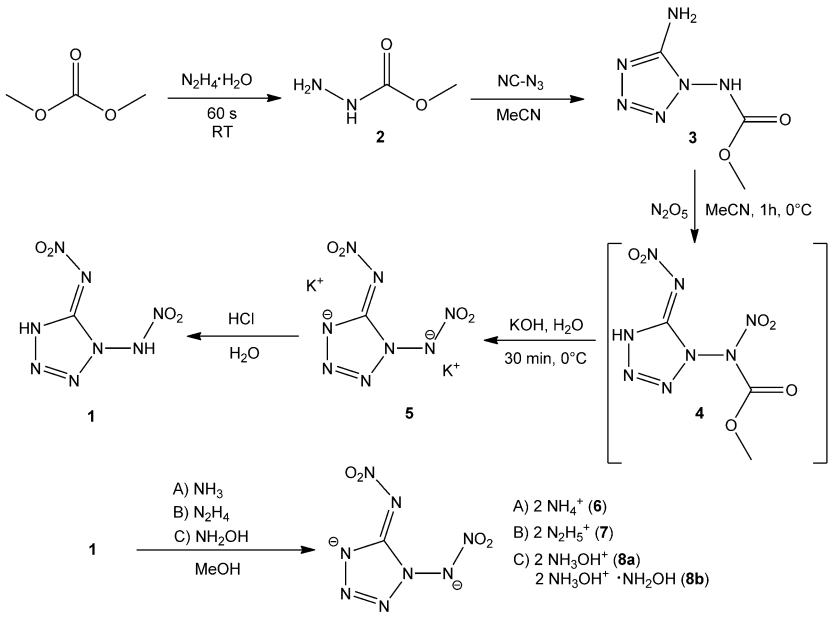

Scheme 2. Synthesis of 1,5-di(nitramino)tetrazole as well as its potassium and selected nitrogen-rich salts.

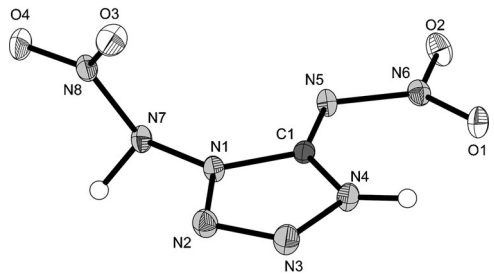

Figure 1. Molecular structure of **1**, showing the atom-labeling. Ellipsoids are set at 50% probability.

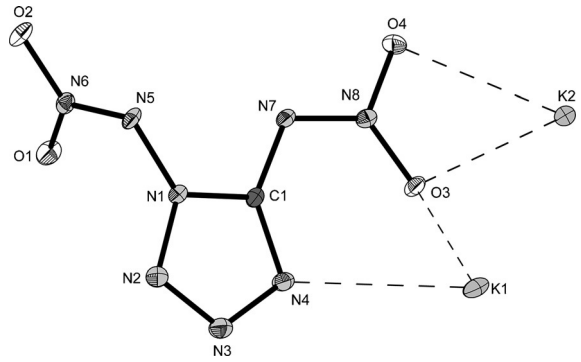

Figure 2. Representation of the molecular unit of **5**. Ellipsoids are set at 50% probability.

almost planar with the ring (⩞C1-N7-N8-O3 2.73(2)°) and the *N*-nitramino moiety is twisted out of the ring plane by 99.3°. The N5–N6 bond (1.331(3) Å) is shorter than in **1** as well as the bond length between N7 and N8 (1.314(3) Å).

The diammonium (**6**) and dihydrazinium salt of 1,5-di(nitramino)tetrazole crystallize in common space groups (**6**: monoclinic, $P2_1/c$; **7**: triclinic, $P\bar{1}$). The densities at 173 K are observed in the same range of (**6**: 1.730; **7**: 1.709 g cm^{-3}). The molecular units are displayed in Figure 3. The bond lengths and angles are similar to those observed for **5**.

The dihydroxylammonium salt was obtained with two different stoichiometries. Crystallization from water yields solvent free **8a** which crystallizes in the triclinic space group $P\bar{1}$ and a density of 1.848 g cm^{-3} at 173 K (Figure 4, left). Additional hydroxylamine leads to a hydroxylamine adduct **8b** which crystallizes in the form of an ammonia oxide (Figure 4, right). **8b** crystallizes in the monoclinic space group $P2_1/c$ with four molecular units in the unit cell and a density of 1.853 (173 K), which is slightly higher than that of **8a.**

Salts **6–8** violently exploded in the DSC sample containers at temperatures of 130 °C (**8a**,**b**), 150 °C (**7**), and 170 °C (**6**). Ca. 1 mg of **1** even destroyed the PT1000 sensor at a temperature of 110 °C. Compound **5** is the most thermally stable salt with a decomposition point of 240 °C. None of the compounds melted before decomposition.

Compound **1** and its salts **5–7** and **8a** are ***very sensitive*** compounds. The measured sensitivity values (according to the German BAM) can be seen in Table 1. The impact sensitivities are in the range of 1 J, which is comparable to the impact

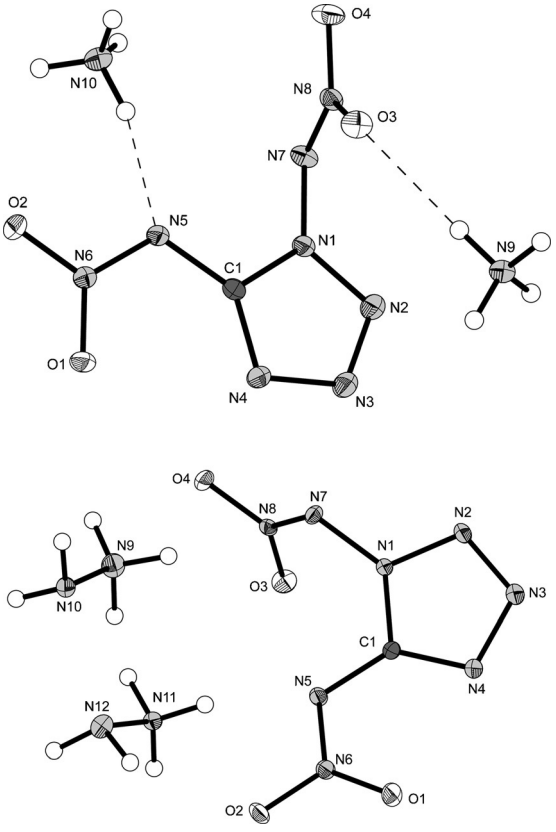

Figure 3. Molecular structures of salts **6** (top) and **7** (bottom). Ellipsoids are set at 50% probability.

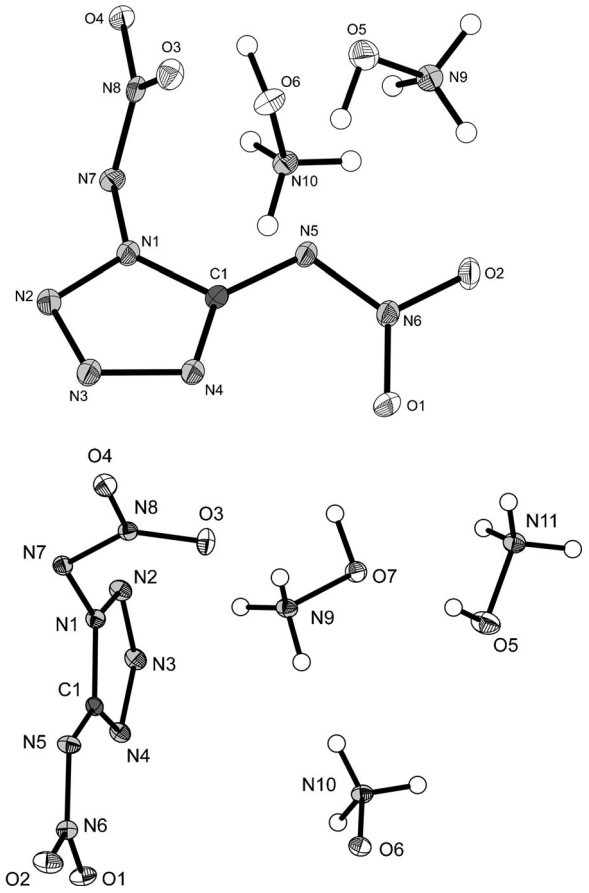

Figure 4. Molecular structures of hydroxylammonium salts **8a** (top) and **8b** (bottom). Ellipsoids are set at 50% probability.

sensitivity of lead azide, and the friction sensitivities are also quite low (<30N). The compounds should therefore be classified as primary explosives. Except for the potassium salt, **1** and its nitrogen-rich salts have highly positive calculated enthalpies of formation (for example, **1**: 508.6, **7**: 573.5 kJ mol^{-1}). Details on the computations are given in the Supporting Information.

As shown in Table 1, compound **1** and its salts **6–8a** have also very high calculated (EXPLO5 6.02)[9] detonation velocities and pressures even close to 10000 m s^{-1} and 434 kbar, which makes them powerful explosives. For comparison, the corresponding values for CL-20 (hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) are listed, which is probably still the benchmark for explosives with respect to performance.[10] Potassium salt **5** shows very promising performance values ($V_{det} > 10000$ m s^{-1}, $p_{CJ} > 500$ kbar). Therefore its use as ingredient in primary explosives was investigated. In the test (Figure 5), about 50 mg of **5** were initiated using a standard pyrotechnical igniter. The shock-wave produced by **5** was easily strong enough to detonate 500 mg of hexogen (RDX).

The test was repeated with 50 mg **5** without RDX. Only a very small dent in the copper plate was observed, which is displayed in the Supporting Information.

It can be concluded that 1,5-di(nitramino)tetrazole (**1**) is one of the most powerful explosives synthesized to date, however the use will be limited owing to its low decomposition point and high sensitivities. Its potassium salt **5** is stable up to 240 °C and shows ideal behavior for use in primary compositions. We recommend using **5** as an environmentally benign and thermally stable sensitizer for example in place of tetracene.[11]

Experimental Section

1-Methoxycarbonyl-1,5-diaminotetrazole (**3**): Methylcarbazate (1.65 g, 18 mmol) in water (10 mL) was added to a freshly prepared solution of cyanogen azide in acetonitrile (20 mmol in 50 mL) at RT. After stirring at RT for one day, the solution was left for crystallization. After most of the acetonitrile was gone, the partially crystalline residue was suspended in 5 mL ice–water and stirred until a white filterable suspension has formed. The suspension was filtered and washed with a little ice–water. The product was dried in air and 1.08 g (37%) of colorless **3** was obtained. IR (ATR): $\tilde{\nu}$ = 3365 (w),

Table 1: Energetic performance parameters of **1**, **5–7**, and **8a**.

	1	**5**	**6**	**7**	**8a**	**CL-20**
Formula	$CH_2N_8O_4$	$CK_2N_8O_4$	$CH_8N_{10}O_4$	$CH_{10}N_{12}O_4$	$CH_8N_{10}O_6$	$C_6H_6N_{12}O_{12}$
IS[a] [J]	1	1	1.5	1	1.5	4[10]
FS[b] [N]	<5	<5	30	6	10	48[10]
N + O[c] [%]	92.62	66.12	91.04	91.31	92.16	82.18
Ω_{CO}; Ω_{CO_2}[d] [%]	16.84; 8.42	−6.02; −12.03	−7.14; −14.27	−12.59; −18.88	6.25; 0	10.95; −10.95
T_{dec}[e] [°C]	110	240	170	150	130	221
ρ[f] [g cm^{-3}]	1.968 (173 K)	2.177 (173 K)	1.730 (173 K)	1.779 (173 K)	1.847 (173 K)	2.083 (100 K)[12]
	1.93 (298 K)	2.137 (298 K)	1.698 (298 K)	1.746 (298 K)	1.813 (298 K)	2.04 (298 K)[10]
$\Delta_f H°$[g] [kJ mol^{-1}]	486.3	−112.4	212.0	541.3	351.5	365.4
$\Delta_f U°$[h] [kJ kg^{-1}]	2649.6	−366.8	1067.4	2256.5	1488.3	918.7
EXPLO6.02 values:						
$-\Delta_{ex}U°$[i] [kJ kg^{-1}]	5921	3938	5240	6082	6619	6168
P_{CJ}[j] [kbar]	434	522	315	376	399	444
V_{det}[k] [m s^{-1}]	9967	10011	9078	9872	9807	9730
V_0[l] [L kg^{-1}]	836	413	978	1003	951	715

[a] Impact sensitivity, BAM drophammer (method 1 of 6). [b] Friction sensitivity, BAM friction tester (method 1 of 6). [c] Summated nitrogen and oxygen content. [d] Oxygen balance. [e] < temperature of decomposition according to DSC (onset temperatures at heating rates of 5 deg min^{-1}); [f] X-ray densities at 173 K and the corresponding RT values calculated using the equation ($\rho_{298K} = \rho_T/(1+\alpha_V(298-T_0))$; $\alpha_V = 1.5\times10^{-4}$ K^{-1}). [g] Heat of formation. [h] Energy of formation. [i] Heat of detonation. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of gases after detonation.

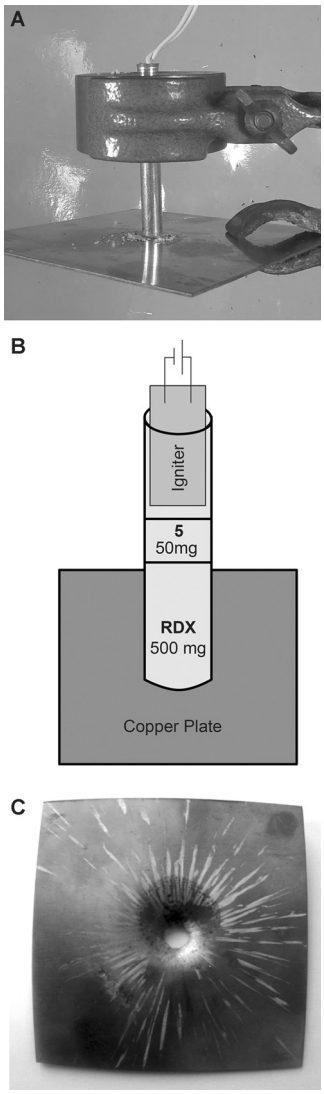

Figure 5. Detonation test using 50 mg **5** and 500 mg RDX and a conventional pyrotechnical igniter. A) Picture of the test setup; B) representation of the test setup; C) perforated copper plate as the result of RDX detonation.

3310 (w), 3258 (w), 3197 (w), 3095 (w), 2863 (w), 1740 (s), 1650 (vs), 1579 (w), 1483 (w), 1448 (m), 1322 (s), 1197 (w), 1117 (m), 1065 (s), 986 (m), 924 (w), 828 (m), 756 (m), 742 (m), 720 (w), 686 (w), 667 cm^{-1} (w); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3257 (9), 3195 (18), 2964 (48), 2864 (15), 1747 (17), 1654 (30), 1580 (21), 1510 (8), 1485 (35), 1460 (9), 1338 (85), 1199 (9), 1119 (51), 1071 (16), 988 (43), 926 (41), 832 (100), 773 (43), 757 (53), 668 (9), 521 (26), 450 (33), 372 (29), 318 cm^{-1} (11); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.21, 7.06, 3.72 ppm; ^{13}C NMR{^{1}H} (400 MHz, [D$_6$]DMSO, 25 °C) δ = 155.2, 155.1, 53.7 ppm; EA calcd for $C_3H_6N_6O_2$ (158.06 g mol^{-1}): C 22.79, H 3.82, N 53.15 %; found: C 23.26, H 3.91, N 51.38 %.

1,5-Di(nitramino)tetrazole (**1**): **3** (1.58 g, 10 mmol) was suspended in dry acetonitrile (30 mL) at 0 °C. N_2O_5 (3.24 g, 30 mmol) in acetonitrile (30 mL) was added in one portion and the mixture was stirred at 0 °C for one hour. The reaction was vigorously stirred and quenched by adding KOH (3.36 g, 60 mmol) dissolved in water (30 mL). The aqueous phase was separated and the water was evaporated under high vacuum. The residue was stirred in methanol (50 mL) for a few hours. The white precipitate consisting of pure KNO_3 and K_2DNAT was filtered, washed with a little methanol, and dried. The solid was dissolved in HCl (30 mL, 2 M) and extracted with four portions of ethylacetate (4 × 20 mL). The solvent was removed from the organic phase in vacuo at RT and the colorless crystalline product was dried in high vacuum to give 950 mg (50 %) of colorless **1**. DSC (5 °C min^{-1},°C): 110 °C (dec.); IR (ATR): $\tilde{\nu}$ = 2967 (w), 2757 (w), 1636 (w), 1591 (vs), 1502 (s), 1304 (s), 1222 (s), 1136 (m), 1022 (m), 1006 (m), 964 (m), 886 (w), 836 (m), 773 (m), 695 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3101 (7), 1614 (17), 1596 (43), 1425 (45), 1320 (36), 1260 (100), 1139 (8), 1025 (11), 1011 (26), 979 (68), 891 (16), 841 (26), 781 (16), 762 (26), 632 (9), 492 (45), 418 (43), 315 (29), 284 (49), 217 cm^{-1} (10); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): δ = 11.91 ppm; ^{13}C NMR{^{1}H} (400 MHz, [D$_6$]DMSO, 25 °C) δ = 147.6 ppm; EA calcd for $CH_2N_8O_4$ (190.02 g mol^{-1}): C 6.32, H 1.06, N 58.95 %; found: C 7.29, H 1.39, N 57.14 %; BAM drophammer: 1 J (< 100–500 μm); friction tester: < 5 N (< 100–500 μm); ESD: 0.3 J.

The synthesis of salts **5**–**8** as well as the general methods are described in the Supporting Information.

Keywords: energetic materials · nitramines · sensitivity · structure elucidation · tetrazoles

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5-Nitriminotetrazole 1-Oxide: An Exciting Oxygen- and Nitrogen-Rich Heterocycle

Dennis Fischer,[a] Thomas M. Klapötke,*[a] and Jörg Stierstorfer[a]

Keywords: Energetic materials / Nitramines / Nitrogen heterocycles / Structure elucidation / Decomposition

5-Nitriminotetrazole 1-oxide ($CH_2N_6O_3$) and selected salts (e.g., dipotassium, diammonium, dihydroxylammonium) were prepared and characterized for the first time. The neutral molecule can be obtained by nitration of an *O*-protected 5-aminotetrazole 1-oxide. The new compounds were characterized by using low-temperature X-ray diffraction as well as IR, Raman, and multinuclear NMR spectroscopy and elemental analysis. Differential scanning calorimetry measurements showed a large range for the decomposition temperatures. The highest value of 320 °C was observed for the dipotassium salt. The energetic performances (detonation velocities up to 9842 m s^{-1}) were calculated with the EXPLO5 code by using calculated (CBS-4M) heats of formation and experimentally obtained X-ray densities. Calculated performance data support the highly energetic character of these new compounds. The sensitivities toward impact, friction, and electrostatic discharge were also determined.

Introduction

The importance of tetrazole *N*-oxides in the field of energetic materials chemistry has increased considerably over the past few years, as tetrazole *N*-oxides often possess higher densities and oxygen balances, and therefore improved energetic performances. Several tetrazole 1-oxides and tetrazole 2-oxides have been prepared, and their energetic properties have been investigated. These materials include 5-nitrotetrazole 2-oxide,[1] 5,5′-bistetrazole 1,1′-dioxide and its dihydroxylammonium salt (TKX-50),[2] and, in particular, 5-aminotetrazole 1-oxide,[3] 5,5′-azo-tetrazole dioxide,[3] and several other 5-substituted tetrazole 1-oxides[4,5] (Figure 1). 5-Nitriminotetrazole is an important energetic molecule that has received attention from several research groups across the world and has been converted into many derivatives. Recently prepared examples are 1-amino-5-nitriminotetrazole[6] and 1,5-di(nitramino)-tetrazole.[7] Also, several O-alkylated 5-nitriminotetrazoles are known.[8]

We have now prepared nonalkylated 5-nitriminotetrazole 1-oxide (**1**) and several salts by double deprotonation of **1** and investigated their use as energetic materials. Compound **1** can act as a mono- or diprotic acid or as a highly energetic ligand and can also be derivatized by alkylation.

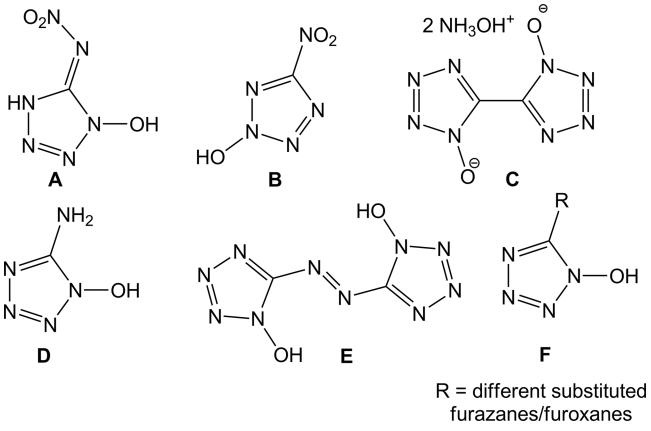

Figure 1. (a) Title compound 5-nitriminotetrazole 1-oxide (**1**) and known tetrazole oxides (b) 5-nitrotetrazole 2-oxide,[1] (c) TKX-50,[2] (d) 5-aminotetrazole 1-oxide,[3] and (e) 5,5′-azotetrazole 1,1′-dioxide.[3] (f) Other substituted tetrazole 1-oxides.[4,5]

Results and Discussion

The synthesis of **1**, shown in Scheme 1, starts with a solution of cyanogen azide, which is treated with hydroxylamine to form 5-amino-1-hydroxytetrazole (**2**).[3] Given that both the direct nitration of **2** and the direct oxidation of 5-nitriminotetrazole always resulted in decomposition, another reaction path was explored. Sodium salt **3**, which was easily formed by deprotonation of **2**, was treated with ethyl chloroformate to yield protected derivative **4**. Derivative **4** was then gently nitrated with N_2O_5 in acetonitrile. Resulting nitrimine **5** was then deprotected in solution by using aqueous KOH without its prior isolation. Evaporation of the liquid phase gave a solid, from which **1** was isolated by acidification and extraction into organic solvents such as ethyl acet-

[a] Department of Chemistry, Ludwig Maximilian University, Butenandtstrasse 5–13 (D), 81377 München, Germany
E-mail: tmk@cup.uni-muenchen.de
www.hedm.cup.uni-muenchen.de

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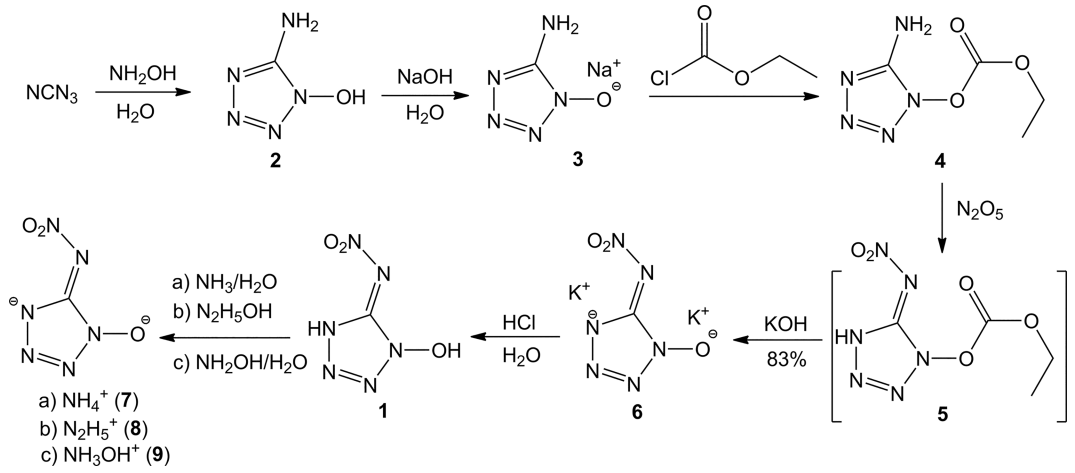

Scheme 1. Synthesis of 5-nitriminotetrazole 1-oxide (**1**) and salts **6**–**10**.

ate. Finally, pure dipotassium salt **6** was precipitated from a methanol solution with KOH. Although acid **1** was obtained in the solid state under high vacuum, attempts to recrystallize **1** in air never resulted in a solid product.

Ammonium salt **7**, hydrazinium salt **8**, hydroxylammonium salt **9**, and potassium salt **10** were prepared by dissolving **1** in methanol and by adding an aqueous solution containing the corresponding base.

Low-temperature X-ray diffraction was used to characterize compounds **3**, **4** (see the Supporting Information), and **6**–**9**. This technique also provided accurate densities for the energetic performance calculations. Salts **7** and **8** were only obtained as crystalline substances with the inclusion of one water solvent molecule. Dipotassium 5-nitriminotetrazole 1-oxide (**1**) crystallizes in the triclinic space group $P\bar{1}$ with a density of 2.270 g cm^{-3} at 173 K. All of the doubly deprotonated salts have similar structures. Bond lengths are given for one example in the caption of Figure 2. The anion is nearly planar [∠C1–N5–N6–O2 = 0.7(9)°, Figure 2]. In all of the structures, the *N*-oxide points in the opposite direction to the nitramino group. Salts **7**–**9** all crystallize in monoclinic space groups (**7**: *Pn*, **8**: $P2_1/c$, **9**:

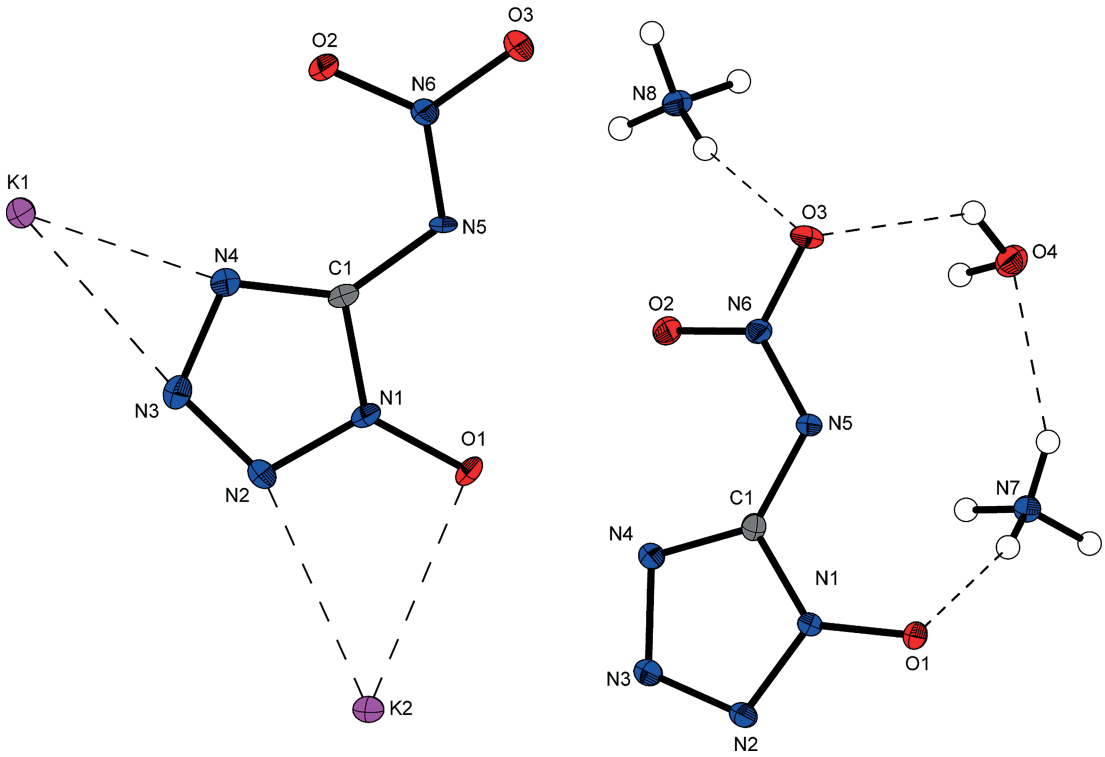

Figure 2. Molecular structures of **6** and **7**·H_2O showing the atom-labeling scheme. Thermal ellipsoids in all structures represent the 50% probability level. Selected bond lengths for **7**·H_2O [Å]: O1–N1 1.327(2), O2–N6 1.253(2), O3–N6 1.266(2), N1–N2 1.342(2), N1–C1 1.348(2), N2–N3 1.311(2), N3–N4 1.357(2), N4–C1 1.336(2), N5–N6 1.313(2), N5–C1 1.386(2).

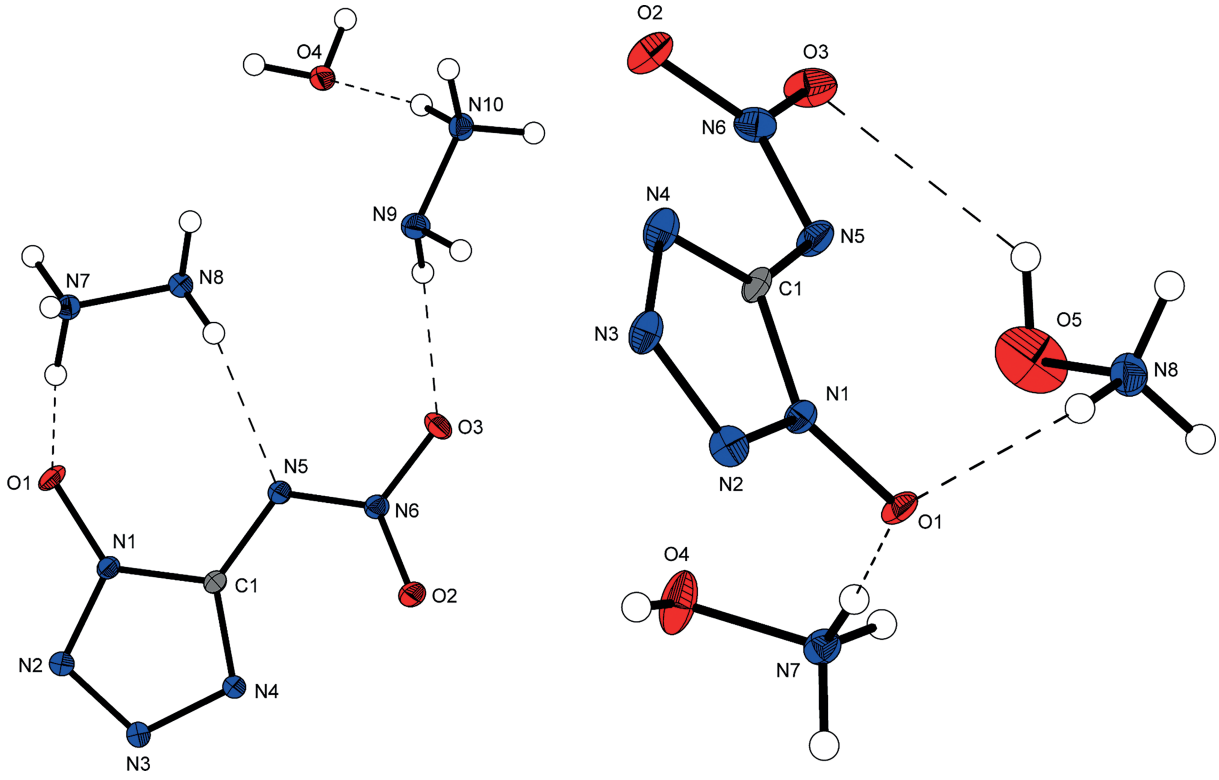

Figure 3. Molecular structures of dihydrazinium salt **8**·H_2O and dihydroxylammonium salt **9**.

Cc). As expected, water-free **9** shows the highest density at 173 K (**7**: 1.724 g cm^{-3}, **8**: 1.706 g cm^{-3}, **9**: 1.789 g cm^{-3}) of the investigated salts (Figure 3).

Differential scanning calorimetry (DSC) measurements for compounds **6**–**10** were performed at a heating rate of 5° min^{-1} and are shown in Figure 4. Compound **6** possesses a remarkably high decomposition temperature of 320 °C, whereas high-nitrogen-content salts **7**, **8**, and **9** decompose at 150, 160, and 130 °C, respectively. Mono-deprotonated potassium salt **10** decomposes at 125 °C, which is almost 200 °C lower than the decomposition temperature of **6**. For the DSC measurements, anhydrous **6**–**10** were used, which were obtained by precipitation from methanol. Compound **6** was also tested for its long-time stability at 260 °C by thermogravimetric analysis (TGA). It stayed unchanged for 33 h. Afterwards, significant decomposition was observed.

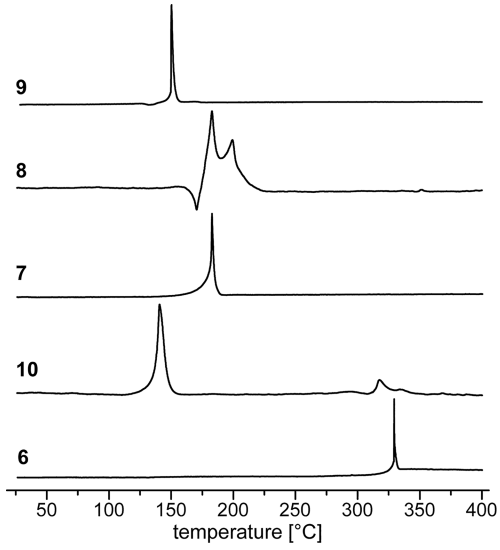

Figure 4. DSC plots of **6**–**10** at 5 °C min^{-1} (exotherm up).

Several calculated (EXPLO5 6.03)[9] and observed energetic properties of **6**–**9** are summarized in Table 1. The detonation velocities of salts **7**–**9** are remarkably high and reach values of 9400–9850 m s^{-1}. The volumes of the gaseous detonation products are also high with values around 1000 L kg^{-1}. The detonation velocity of potassium salt **6** was calculated to be 7846 m s^{-1}, which appears to be a more realistic value than the values observed with the previous EXPLO5 versions. The density of anhydrous **8** was estimated to be 1.67 g cm^{-3}, as only the crystal structure of the monohydrate (ρ = 1.706 g cm^{-3} at 173 K) was obtained. Compound **6** appears to be insensitive to friction, impact, and electrostatic discharge followed by **7**, which is not completely insensitive. Compounds **8** and **9** have sensitivities comparable to that of pentaerythritol tetranitrate. The sensitivity values of **6**–**10** were measured according to the German BAM by using a drophammer as well as a friction device. Values over a very broad range were obtained. Whereas **6** is insensitive towards impact and friction, **9** has to be ranked as very sensitive.

Table 1. Energetic performance parameters of **6**–**9**.

	6	**7**	**8**	**9**
Formula	$CK_2N_6O_3$	$CH_8N_8O_3$	$CH_{10}N_{10}O_3$	$CH_8N_8O_5$
IS[a] [J]	>40	10	6	3
FS[b] [N]	>360	260	80	72
ESD[c] [J]	>1.5	>1.5	0.2	0.2
Ω_{CO}; Ω_{CO_2}[d] [%]	+7.20; 0	–17.8; –26.6	–22.84; –30.45	0; –7.54
T_{dec}[e] [°C]	320	150	160	130
ρ[f] [g cm^{-3}]	2.270 (173 K), 2.228 (298 K)	1.75 (298 K)	1.67 (est.)	1.706 (173 K), 1.675 (298 K)
$\Delta_f H°$[g] [kJ mol^{-1}]	–280.0	27.4	491.8	491.8
$\Delta_f U°$[h] [kJ kg^{-1}]	–1261.0	282.9	2475.7	2475.7
EXPLO6.03 values				
$-\Delta_{ex} U°$[i] [kJ kg^{-1}]	3273	4259	5999	7622
P_{CJ}[j] [kbar]	240	334	366	373
V_{det}[k] [m s^{-1}]	7846	9475	9842	9602
V_0[l] [L kg^{-1}]	281	996	1017	969

[a] Impact sensitivity, BAM drophammer (method 1 of 6). [b] Friction sensitivity, BAM friction tester (method 1 of 6). [c] Electrostatic discharge device (OZM research). [d] Oxygen balance. [e] Temperature of decomposition according to DSC (onset temperatures at heating rates of 5° min^{-1}). [f] X-ray density at 173 K and the corresponding room temperature value calculated by using the equation $\rho_{298\,K} = \rho_T/[1 + \alpha_V(298–T_0)]$; $\alpha_V = 1.5\times10^{-4}$ K^{-1}. [g] Heat of formation. [h] Energy of formation. [i] Heat of detonation. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of gases after detonation.

Conclusions

In terms of thermal stability and sensitivity, it can be concluded that the 5-nitriminotetrazole 1-oxide system is comparable to its parent non-oxide. It can be synthesized by simple nitration of 5-aminotetrazole 1-oxide after protecting the N-hydroxy function. All of the salts that were investigated so far show low thermal stability, except for the dipotassium salt (decomposition temperature: 320 °C). It can be concluded that **1** is an interesting new heterocycle that can be used for many different investigations in the future, for example, as a high-energy-capacity ligand in energetic coordination complexes or in alkaline and alkaline earth metal salts as high-energy fuels for pyrotechnic applications.

Experimental Section

General Methods: See the Supporting Information.

***O*-Ethoxycarbonyl-5-aminotetrazole 1-Oxide (4):** Sodium 5-aminotetrazole 1-oxide (**3**; 12.3 g, 100 mmol, precipitated from 5-aminotetrazole 1-oxide and NaOH in EtOH) was suspended in dry acetonitrile (200 mL). Ethyl chloroformate (10.8 g, 100 mmol) was added in one portion, and the mixture was stirred for 3 h at room temperature. The precipitated NaCl was filtered off, and the filtrate was concentrated in vacuo. Diethyl ether (20 mL) was added, and the mixture was stirred until a white precipitate formed. The suspension was filtered at –20 °C and was washed with a few drops of cold diethyl ether. Colorless 5-amino-*O*-ethoxycarbonyl-tetrazole 1-oxide was obtained (5.2 g, 30%). The residual 5-aminotetrazole oxide was recycled by boiling in 1 M HCl and evaporating the solvent. ^{1}H NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 6.26, 4.17 (q), 1.26 (t) ppm. ^{13}C{^{1}H} NMR (400 MHz, [D$_6$]acetone, 25 °C): δ = 153.3, 151.2, 64.0, 13.8 ppm. IR (ATR): $\tilde{\nu}$ = 3315 (w), 3266 (w), 3296 (w), 3153 (w), 1815 (s), 1661 (s), 1599 (m), 1473 (w), 1445 (w), 1394 (w), 1370 (w), 1310 (w), 1300 (w), 1208 (vs), 1157 (w), 1111 (w), 1087 (m), 1018 (w), 977 (w), 943 (m), 887 (m), 798 (w), 762 (m), 746 (w), 727 (w) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 3322 (2), 3268 (3), 3142 (14), 2993 (7), 2981 (32), 2946 (60), 2933 (4), 2877 (5), 2783 (4), 2734 (5), 1816 (18), 1660 (13), 1595 (9), 1475 (4), 1447 (19), 1399 (5), 1316 (64), 1168 (7), 1132 (26), 1110 (9), 1086 (10), 1019 (5), 982 (25), 949 (5), 890 (100), 799 (58), 764 (6), 747 (16), 704 (11), 513 (25), 351 (55), 319 (20), 286 (16) cm^{-1}. $C_4H_7N_5O_3$ (173.13): calcd. C 27.75, H 4.08, N 40.45; found C 27.83, H 3.98, N 40.37.

Dipotassium 5-Nitriminotetrazole 1-Oxide (6): 5-Amino-*O*-ethoxycarbonyl-tetrazole 1-oxide (1.73 g, 10 mmol) was dissolved in dry acetonitrile (40 mL). N_2O_5 (1.4 g, 13 mmol) was added at 0 °C, and the solution was stirred for 10 min at 0 °C. A solution of KOH (2 g, 36 mmol) in water (10 mL) was added in one portion, and the mixture was vigorously stirred at room temperature for 30 min. The solvent was removed in vacuo, and the residue was stirred in MeOH (30 mL) for 1 h. The solid was filtered off and dissolved in 4 M HCl (50 mL). 5-Nitriminotetrazole 1-oxide was extracted with ethyl acetate (5 × 20 mL). The solvent of the organic phase was removed under high vacuum at room temperature, which yielded an orange solid. MeOH (20 mL) was added, followed by an excess amount of KOH in MeOH. The orange solid that precipitated was filtered off, washed with a small amount of methanol, and dried in air to afford dipotassium 5-nitriminotetrazole 1-oxide (1.84 g, 83%). DSC (5 °C min^{-1}): 325 °C (dec.). IR (ATR): $\tilde{\nu}$ = 1633 (w), 1492 (s), 1400 (m), 1379 (s), 1360 (s), 1336 (vs), 1255 (w), 1250 (w), 1236 (s), 1158 (w), 1032 (s), 885 (m), 760 (m), 721 (m) cm^{-1}. Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}$ = 1497 (100), 1459 (7), 1415 (5), 1379 (10), 1320 (5), 1251 (15), 1240 (3), 1160 (3), 1120 (4), 1037 (16), 993 (12), 887 (4), 723 (3), 417 (2), 322 (6) cm^{-1}. MS (FAB–): *m*/*z* = 145.1 ($CHN_6O_3^-$). $CK_2N_6O_3$ (221.93): calcd. C 5.40, H 0, N 37.81; found C 5.51, H 0, N 35.32. BAM drophammer: >40 J (<100 μm); friction tester: >360 N (<100 μm); ESD >1.5 J.

Supporting Information (see footnote on the first page of this article): Experimental procedures and analytical data for **7**–**10**.

Acknowledgments

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Tetranitratoethane†

Dennis Fischer, Thomas M. Klapötke* and Jörg Stierstorfer

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Tetranitratoethane ($C_2H_2N_4O_{12}$), which has an oxygen content of 70.1% was synthesized by nitration of monomeric glyoxal using N_2O_5 and purified by sublimation. Single crystals could be grown from CH_2Cl_2/pentane and were used to determine the structure by X-ray diffraction. Several energetic parameters and values were also established.

In the continuous worldwide quest for new oxidizers in order to replace ammonium perchlorate due to its toxicity for humans' thyroids a few derivatives with a sufficiently high oxygen balance were published during the last years. A few of them are displayed in Fig. 1: (A) tetranitroacetimidic acid,[1] (B) nitryl cyanide,[2] (C) trinitramine[3] and fluorodinitramine,[4] and (D) 2,2,2-trinitroethyl nitrocarbamate.[5]

In general an oxidizer is a material with a positive oxygen balance Ω, having the ability to form additional O_2 besides H_2O, N_2, CO/CO_2 during its combustion. The absolute oxygen balance Ω, is the ratio between the amount of active available oxygen divided by the overall mass of oxidizer material. Ω is usually given in % w/w and can be calculated assuming different combustion products *e.g.* CO_2 or CO (see footnote Table 1). In this contribution we report on tetranitratoethane, a new solid state oxidizer, which has a higher oxygen content than prominent solid examples such as ADN (ammonium dinitramide), $KClO_4$, NH_4ClO_4, tetranitroacetimidic acid and even tetranitromethane. Compound **1** is a geminal dinitrato alkane. While nitrate esters such as nitroglycerin (NG) and pentaerythritoltetranitrate (PETN) (Fig. 2A and B) are well known only very few examples of geminal C-nitrato compounds are known. The simplest one, dinitratomethane (Fig. 2C) is a liquid which is obtained from nitration of 1,3,5-trioxane in a HNO_3/H_2SO_4 mixture.[6]

Gemial dinitrate esters form during the nitration of the geminal diol form of aldehydes. They can be also obtained *via* the addition of N_2O_5 to the double bond of aldehydes like **1** is obtained from monomeric glyoxal.‡ A stream of monomeric glyoxal was introduced into a solution of N_2O_5 in acetonitrile at ice bath temperature (Scheme 1). After a few minutes the reaction was poured on ice and crude **1** separated as an oily liquid. The mixture was extracted with CH_2Cl_2. After removing the solvent crude **1** was obtained as an oil which solidified on standing. The material was purified by sublimation at 70 °C under high vacuum against dry ice. The crystals of the crude material melt at 62 °C before sublimation takes place.

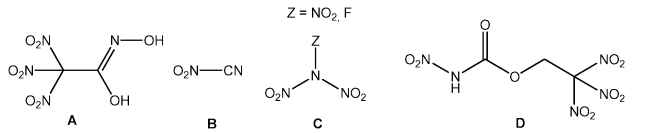


Fig. 1 Structural formula of tetranitroacetimidic acid (A), nitryl cyanide (B), trinitramine and fluoronitramine (C) as well as 2,2,2-trinitroethyl nitrocarbamate (D).

The purified material is stable at room temperature under a dry atmosphere. In air it slowly hydrolyses forming nitric acid and glyoxal again. The hydrolysis however is slow enough to prevent the material from being hydrolyzed in ice water after quenching the reaction. The pure material was slowly crystallized from a dry mixture of CH_2Cl_2/pentane in a stream of dry nitrogen. Among others one big (*ca.* 0.4 × 1.0 × 1.0 cm) crystal of **1** was formed over night. The X-ray structure§ reveals the material crystallizing in the orthorhombic space group $P2_1/c$ with a density of 1.991 g cm^{-3} at 173 K (Fig. 3). A DSC with a heating rate of 5 °C indicates the material starting to decompose at 90 °C. NMR spectroscopy in $CDCl_3$ revealed a singlet $^{13}C\{^1H\}$ resonance at 91.3 ppm and a ^1H proton resonance at 7.21 ppm.

Compound **1**, which has a higher oxygen content and balance than ammonium perchlorate (Table 1) is very sensitive toward friction (5 N) and impact (2 J). In terms of sensitivity it is comparable to nitroglycerin and more sensitive than PETN (Table 1). The heat of formation of −385 kJ mol^{-1} was calculated using the atomization method based on CBS-4M electronic enthalpies (see ESI†).

Ludwig Maximilian University Munich, Department of Chemistry, Butenandtstr. 5-13, 81377 München, Germany. E-mail: tmk@cup.uni-muenchen.de; Web: http://www.hedm.cup.uni-muenchen.de; Fax: +49 (0) 89 2180 77492

† Electronic supplementary information (ESI) available: (1) X-ray parameters, (2) heat of formation calculation, (3) experimental. CCDC 1420413. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc09010e

Table 1 Selected physicochemical values of **1**, ammonium perchlorate (AP), nitroglycerine (NG) and pentaerythritol tetranitrate (PETN)

	1	AP	NG	PETN
Formula	$C_2H_2N_4O_{12}$	NH_4ClO_4	$C_3H_5N_3O_9$	$C_5H_8N_4O_{12}$
FW/g mol^{-1}	274.06	117.49	227.09	316.14
IS/J [a]	2	20	0.2	3
FS/N [b]	5	>360	>360	60
N, O% [c]	20.44, 70.06	11.92, 54.47	18.5, 63.41	17.72, 60.73
Ω_{CO}, Ω_{CO_2}/% [d]	+52.54, +40.87	34.04, 34.04	3.5, 24.66	−10.12, 15.18
T_m, T_{dec}/°C [e]	62, 90	—, 240	13, 185	141, 202
ρ/g cm^{-3} (RT) [f]	1.954	1.95	1.595*	1.75*
$\Delta_f H_m^\circ$/kJ mol^{-1} [g]	−384.6	−295.8	−311.3	−479.7
$\Delta_f U^\circ$/kJ kg^{-1} [h]	−1321.9	−2623.2	−1278.1	−1423.3
I_{sp}/s [i]	272.3	263.8	263.8	256.6
I_{sp}/s [j]	265.1	255.9	257.6	241.3
Ox/Al/% w/w [k]	65.44/19.56	65.85/19.15	70.83/14.17	69.83/15.62

[a] Impact sensitivity according to BAM drophammer (1 of 6). [b] Friction sensitivity according to BAM friction tester (1 of 6). [c] Nitrogen and oxygen content. [d] Oxygen balance toward carbon monoxide ($\Omega_{CO} = n$O − xC − yH/2(1600/FW)) and carbon dioxide ($\Omega_{CO_2} = n$O − 2xC − yH/2(1600/FW)). [e] Melting and decomposition temperature (DSC, 5 deg min^{-1}). [f] Density at 298 K (for **1** calculated with: $\rho_{X\text{-ray-}100K}$/1.0297). [g] Heat of formation (calculated using the atomization method and CBS-4M enthalpies). [h] Energy of formation. [i] Optimized specific impulse (Cheetah 6.0, shifting equilibrium, 15% w/w HTPB). [j] Optimized specific impulse (Cheetah 6.0, frozen equilibrium, 15% w/w HTPB). [k] Optimized amounts of oxidizer and aluminum.

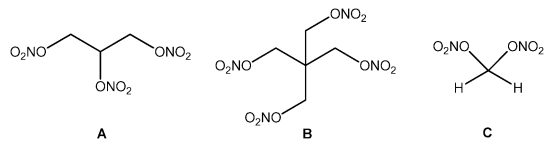
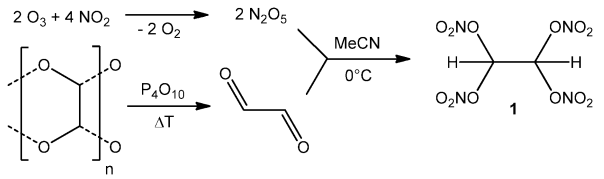


Fig. 2 Structural formula of nitroglycerin (A), PETN (B), and dinitratomethane (C).



Scheme 1 Formation of **1** from glyoxal and N_2O_5.

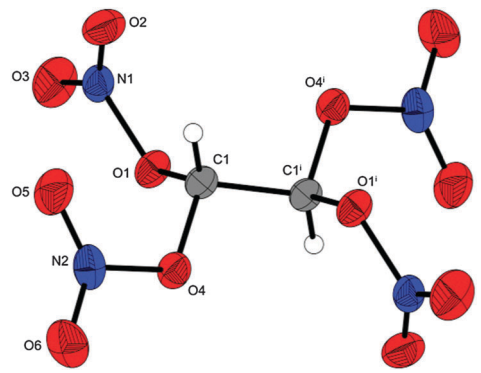


Fig. 3 Molecular structure of **1**. Thermal ellipsoids represent the 50% probability level. Selected bond distances [Å]: O1–C1 1.421(1), O1–N1 1.443(1), O4–C1 1.410(1), O4–N2 1.449(1), O5–N2 1.193(1) O2–N1 1.190(1), O6–N2 1.191(1), N1–O3 1.193(1), C1–C1^i 1.526(2). Symmetry code: (i) 1 − x, −y, 1 − z.

The specific impulse from isobaric combustion calculations of three component (oxidizer, aluminum and HTPB) mixtures with optimized oxidizer to aluminum ratio was calculated using the Cheetah 6.0 code. The mixtures using **1** perform slightly higher (8–9 s) than the ammonium perchlorate mixtures and those containing nitroglycerine and PETN (for theoretical comparison). As a general empirical rule, an increase of the value for the specific impulse by 20 s leads to a doubling of the possible payload of a rocket.[7]

Summarizing all the physicochemical properties of **1**, especially the low thermal stability but also the high sensitivities will probably exclude any practical application of **1**. Nevertheless **1** is a solid oxidizer carrying one of the highest oxygen contents which were ever synthesized.

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU) and the Office of Naval Research (ONR) is gratefully acknowledged. The authors acknowledge Prof. Dr Karl O. Christe for doing the specific impulse calculations.

Notes and references

‡ 5 g of dehydrated and powdered glyoxal were mixed with 15 g of P_4O_{10} and slowly heated in an oil bath to 200 °C in a 50 mL flask until the material turned black. The green vapors were introduced into an ice cooled solution of 15 g N_2O_5 in 50 mL CH_2Cl_2 or CH_3CN. Then the reaction was poured on 100 mL ice water and immediately extracted with four times 50 mL CH_2Cl_2. The organic phase was washed with 1% $NaHCO_3$ until neutral and dried over $MgSO_4$. After carefully (RT) removing the solvent under vacuum the crude material was sublimed at 70 °C under high vacuum against dry ice yielding 7–8 g of a colorless solid. The yield strongly depends on the technique which is used for generating anhydrous glyoxal. Based on monomeric glyoxal the yield is nearly quantitative. DSC (5 °C min^{-1}, °C): 90 °C (dec.); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3000 (w), 2948 (w), 1678 (s), 1664 (s), 1537 (w), 1465 (w), 1342 (w), 1271 (s), 1140 (w), 1048 (m), 989 (s), 821 (m), 771 (vs), 732 (s), 720 (s), 684 (s), 596 (s), 563 (m); Raman (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 2997 (54), 2859 (6), 1729 (6), 1693 (50), 1671 (10), 1465 (6), 1356 (45), 1306 (90), 1278 (13), 1148 (47), 1074 (10), 1014 (15), 855 (100), 790 (6), 778 (14), 757 (11), 734 (8), 675 (64), 626 (22), 579 (53); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): δ = 7.21; ^{13}C NMR{^{1}H} (400 MHz, $CDCl_3$, 25 °C, ppm) δ = 91.3; ^{14}N NMR (400 MHz, $CDCl_3$, 25 °C, ppm) δ = −62.3; EA ($C_2H_2N_4O_{12}$, 174.06): calc.: C 8.77, H 0.74, N 20.44%; found: C 8.97, H 0.83, N 20.19%; BAM drophammer: 2 J (>500 μm); friction tester: <5 N (>500 μm).

§ Selected X-ray parameters: monoclinic, $P2_1/c$, a 7.5489(4) Å, b 7.2995(3) Å, c 8.3759(8) Å, γ 97.93(1)°, V 457.12(5), Z 2, ρ 1.991 g cm^{-3}, CCDC 1420413.

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Energetic Materials

1,1′-Nitramino-5,5′-bitetrazoles

Dennis Fischer, Thomas M. Klapötke,* Jörg Stierstorfer, and Norbert Szimhardt[a]

Abstract: 1,1′-Dinitramino-5,5′-bitetrazole and 1,1′-dinitramino-5,5′-azobitetrazole were synthesized for the first time. The neutral compounds are extremely sensitive and powerful explosives. Selected nitrogen-rich salts were prepared to adjust sensitivity and performance values. The compounds were characterized by low-temperature X-ray diffraction, IR and Raman spectroscopy, multinuclear NMR spectroscopy, elemental analysis, and DTA/DSC. Calculated energetic performances using the EXPLO5 code based on calculated (CBS-4M) heats of formation and X-ray densities support the high performances of the 1,1′-dinitramino-5,5′-bitetrazoles as energetic materials. The sensitivities toward impact, friction, and electrostatic discharge were also explored. Most of the compounds show sensitivities in the range of primary explosives and should only be handled with great care!

Introduction

Modern CHNO explosives consist of a high-heat-of-formation backbone combined with the density-enhancing properties of oxidizing building blocks such as N-oxides or nitro moieties.[1,2] The introduction of these units into tetrazole compounds results in the substitution of the acidic protons with hydroxy or nitramino moieties and is one of the strategies to synthesize highly energetic tetrazole derivatives. Both moieties lead to an increase in explosive performance, but only the hydroxy functionality decreases the sensitivity, whereas the N-nitramino moiety makes even the anions of the molecules highly sensitive toward impact and friction. A few examples are given in Figure 1.

1-Nitraminotetrazoles are of great interest for the design of heavy metal free primary explosives[7] and other energetic ingredients for which increased sensitivities are desired.

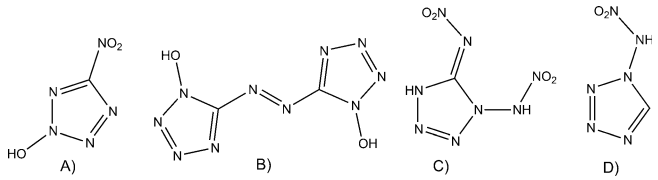

Figure 1. A selection of tetrazoles substituted with hydroxyl or nitramino moieties: A) 2-hydroxy-5-nitrotetrazole,[3] B) 1,1′-dihydroxy-5,5′-azobitetrazole,[4] C) 1,5-dinitraminotetrazole,[5] D) 1-nitraminotetrazole.[6]

Herein, 1,1′-dinitramino-5,5′-bitetrazole (**1**) and selected ionic derivatives are presented as consequence of our ongoing research toward 1-nitraminotetrazoles. Furthermore highly energetic 1,1′-dinitramino-5,5′-azobitetrazole (**2**) was synthesized and its potassium (**4**) and ammonium (**7**) salts were investigated.

Results and Discussion

The neutral compounds **1** and **2** can be isolated from the potassium salts **3** and **4** by acidification and extraction into organic solvents (ethyl acetate was used here). The synthesis and properties of **3**, which is an outstanding primary explosive, have been described recently.[7] Potassium-1,1′-dinitramino-5,5′-azobitetrazolate (**4**) is synthesized by nitration of 1,1′-diamino-5,5′-azobitetrazole[8] and subsequent quenching with KOH. The nitration is carried out with great care in dry acetonitrile below 0 °C with two equivalents of N_2O_5 according to Scheme 1. The addition of the nitrating reagent has to be carried out very slowly since the starting material does not dissolve very well in acetonitrile. An excess of nitrating reagent would cause decomposition of the product. Compound **4** is isolated after quenching with aqueous KOH and subsequent filtering of the potassium salt. Salts **5**–**7** derived from **1** and **2** were synthesized by neutralization of the solution of the parent acid with the appropriate base (Scheme 1). Compound **1** was isolated as a solid and characterized, whereas compound **2** was only isolated once, resulting in a violent detonation.

Crystal structures

During this work, the crystal structures of compounds **1** and **4**–**7** were determined by low-temperature X-ray diffraction. Selected data of the measurements and the refinements are given in the Supporting Information. The crystal structures were deposited in the CSD database.[9]

[a] Dr. D. Fischer, Prof. Dr. T. M. Klapötke, Dr. J. Stierstorfer, N. Szimhardt
Department of Chemistry, Energetic Materials Research
Ludwig Maximilian University
Butenandtstrasse 5–13 (D), 81377 München (Germany)
Fax: (+49) 89-2180-77492
E-mail: tmk@cup.uni-muenchen.de

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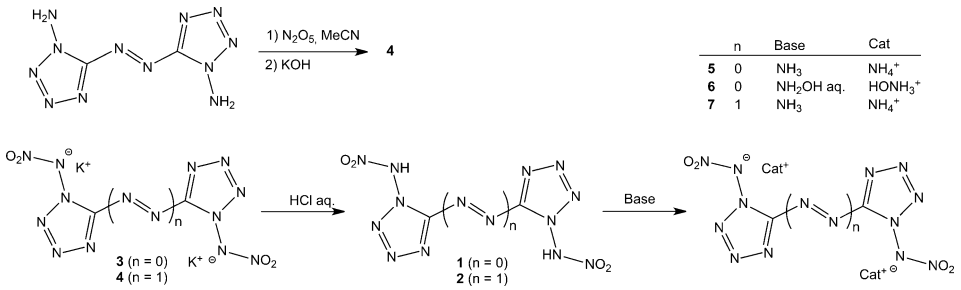

	n	Base	Cat
5	0	NH_3	NH_4^+
6	0	NH_2OH aq.	$HONH_3^+$
7	1	NH_3	NH_4^+

Scheme 1. Synthesis of compounds **1**, **2**, and **4**–**7**.

The parent compound **1**, shown in Figure 2, crystallizes in the monoclinic space group $P2_1/n$ with two molecular moieties in the unit cell. The observed density of 1.967 g cm^{-3} at 173 K is one of the highest ever observed for a CHNO-containing tetrazole derivative. Both tetrazole rings are coplanar. The C–C bond length of 1.44 Å is significantly shorter than a typical C–C single bond (1.54 Å). The nitramino group is strongly twisted out of the ring plane (< N2-N1-N5-N6 111.3°). The nitramine proton is involved in the strong hydrogen bond (N5–H5···N3 0.87(2), 2.16(2), 2.971(2) Å, 155(2)°).

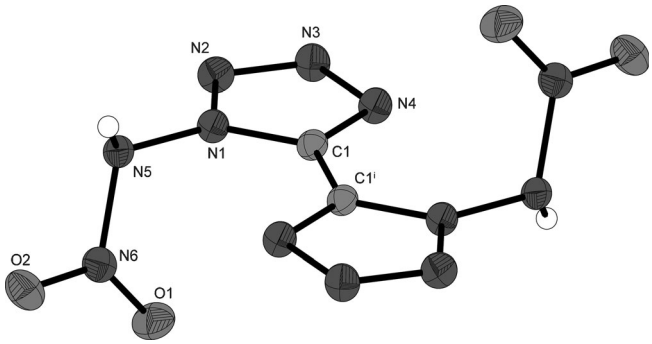

Figure 2. Representation of the molecular unit of 1,1′-dinitramino-5,5′-bitetrazole (**1**), showing the atom labeling scheme. Ellipsoids for non-hydrogen atoms in all crystal structure plots are set at 50% probability.

Bis(ammonium) 1,1′-dinitramino-5,5′-bitetrazolate (**5**) also crystallizes in the monoclinic space group $P2_1/c$. The observed density of 1.848 g cm^{-3} (100 K) is lower than that of **1**. However, it is slightly higher compared to ammonium 5,5′-bitetrazolate dioxide (1.800 g cm^{-3} at 173 K).[10] The nitramino groups again are twisted out from the bitetrazole plane with a torsion angle C1-N1-N5-N6 of 78.5(1)°. Figure 3 shows one molecular anion cation pairing of **5**.

Bis(hydroxylammonium) 1,1′-dinitramino-5,5′-bitetrazolate (**6**) also crystallizes anhydrously from methanol with a slightly higher density of 1.877 g cm^{-3} (173 K) than **6** in the triclinic space group $P\bar{1}$. The molecular unit is shown in Figure 4.

Dipotassium 1,1′-dinitramino-5,5′-azobitetrazolate (**4**) crystallizes with a density of 2.143 g cm^{-3} at 100 K in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. The density is slightly lower than that of potassium 5,5′-azotetrazole dioxide (2.200 g cm^{-3} at 173 K).[4] Figure 5 illustrates the molecular unit. The two ring planes show a torsion angle of 21.6°. Again the nitramine moieties are twisted out of the ring planes (C1-N1-N5-N6 84.41(3)°, C2-N9-N13-N14 87.27(3)°). The N–N bond lengths of the nitramines are 1.402(8) Å (N1–N5) and 1.395(8) Å (N9–N13).

The molecular moiety of diammonium 1,1′-dinitramino-5,5′-azobitetrazolate (**7**), which crystallizes in the triclinic space group $P\bar{1}$, is depicted in Figure 6. The density of **7**

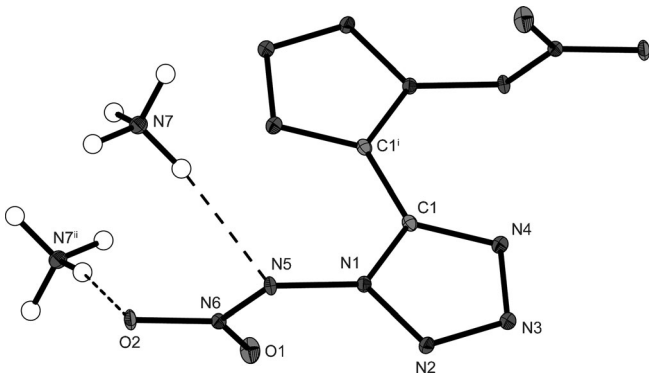

Figure 3. Molecular unit of **5**, showing the atom-labeling scheme. Symmetry codes: (i) 1−*x*, −y, 1−*z*; (ii) −x, −y, 1−*z*.

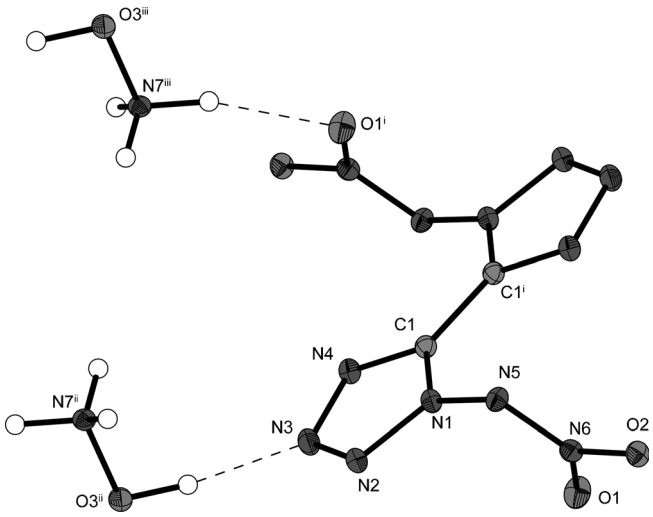

Figure 4. Molecular unit of **6**, showing the atom-labeling scheme. Symmetry codes: (i) −*x*, 2−*y*, 1−*z*; (ii) 1−*x*, 1−*y*, 1−*z*; (iii) x, 1+y, 1+z.

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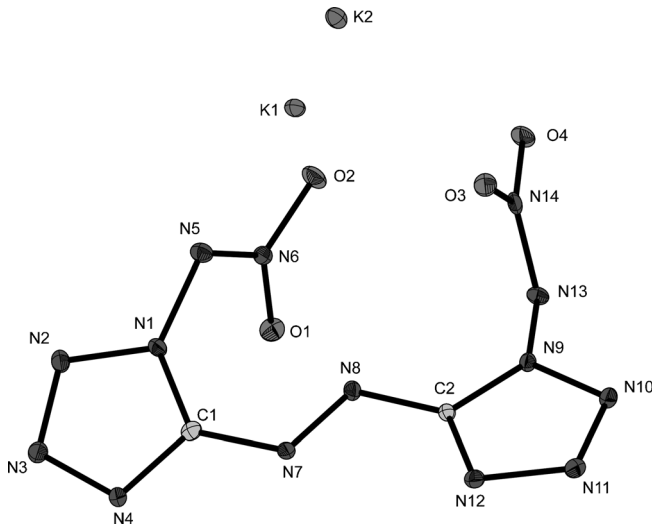

Figure 5. Representation of the molecular unit of **4**, showing the atom labeling scheme.

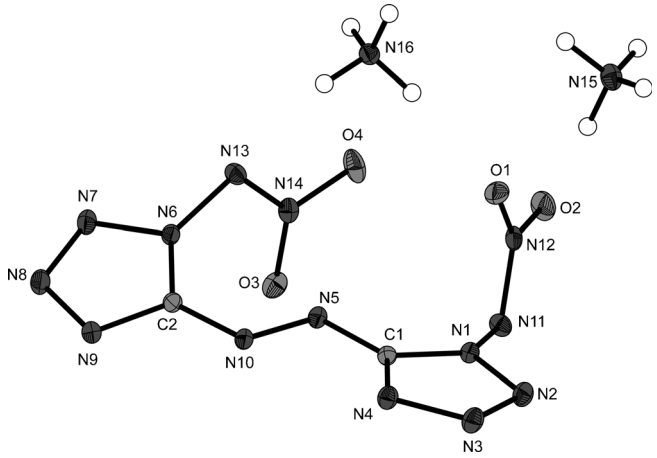

Figure 6. Representation of the molecular unit of **7**, showing the atom labeling scheme.

(1.786 g cm^{-3} at 173 K) is smaller than that observed for ammonium salt **5** and also smaller than that of bis(ammonium) 5,5′-azotetrazole dioxide (1.800 g cm^{-3} at 173 K).[4] The tetrazole rings are not coplanar (N1-C1-C2-N6 28.2(2)°). The N=N azo bond has a length of 1.261(2) Å, which is slightly longer than typical N=N double bonds (1.20 Å). In accordance to the structure of **4**, both nitramino groups are on one side of the dianion. All protons of the ammonium cations participate in hydrogen bonds.

Physicochemical properties

Since all materials investigated are highly energetic compounds, their physicochemical properties were explored.

Thermal behavior

The thermal behavior of compound **1** was investigated using DTA (OZM research), showing a violent detonation at 107 °C. Compounds **4**–**8** were investigated on a Linseis PT10 DSC with a heating rate of 5 °C min^{-1} using about 1 mg of material. All 1-nitraminotetrazoles and their salts detonated violently in the DSC, in the case of **4** and **7** with damage to the Pt100 sensor. Compound **2** was too sensitive to measure a DSC curve in a proper way. In general the salts of 1,1′-dinitramino-5,5′-azobitetrazole are less thermally stable than those of 1,1′-dinitramino-5,5′-bitetrazole. Compound **3** decomposes at 200 °C,[7] while **4** is only stable up to 170 °C. The same trend occurs with the ammonium salts **5** and **7**. The latter compound detonated in the DSC, damaging the setup, and therefore only a smaller part of the graph could be recorded (Figure 7).

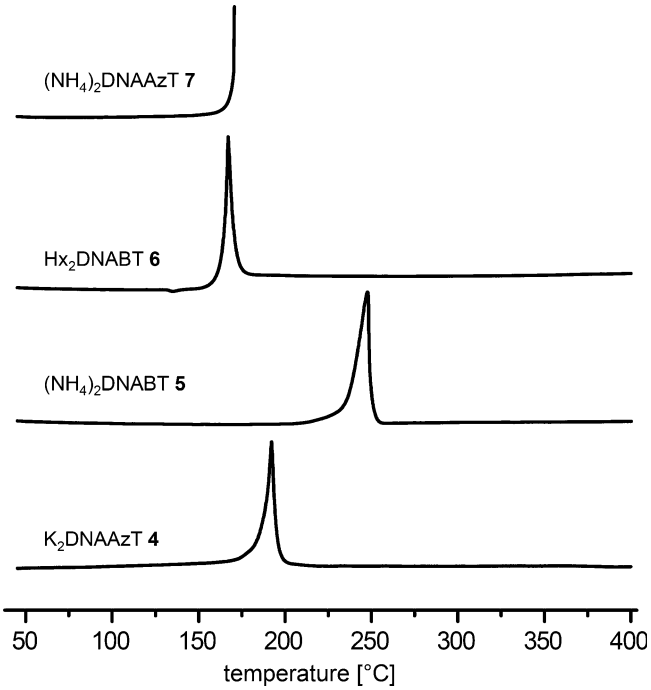

Figure 7. DSC plots of compounds **4**–**7** (*exo*-up, 5 °C min^{-1}).

Heats of formation, sensitivity, and detonation parameters

The heats of formation were calculated theoretically using the atomization Equation (1) and CBS-4M electronic enthalpies described in the Supporting Information. The detonation parameters were calculated with the EXPLO5 6.03 computer code using X-ray densities, which were converted to room-temperature values according to Equation (2). A coefficient of volume expansion[11] α_v of $1.5\cdot10^{-4}$ K^{-1} was used.

$$\Delta_f H^\circ_{(g,M,298)} = H_{(M,298)} - \Sigma H^\circ_{(atoms,298)} + \Sigma \Delta_f H^\circ_{(atoms,298)} \quad (1)$$

$$\rho_{298K} = \rho_T / (1 + \alpha_v (298 - T_0)) \quad (2)$$

The energetic parameters of compounds **1**, **4**, **5**, **6**, and **7** are summarized in Table 1. All compounds are formed endothermi-

Table 1. Energetic performance parameters of **1** and **4**–**7**.

	1	**4**	**5**	**6**	**7**
Formula	$C_2H_2N_{12}O_4$	$C_2K_2N_{12}O_4$	$C_2H_8N_{14}O_4$	$C_2H_8N_{14}O_6$	$C_2H_8N_{16}O_4$
IS[a] [J]	<1	<1	2	2	<1
FS[b] [N]	<5	<5	<5	5	<5
ESD[c] [J]	0.03	0.04	0.2	0.1	0.05
Ω_{CO2}[d] [%]	−6.20	−4.42	−21.90	−9.87	−19.96
T_{dec}[e] [°C]	107	180	210	155	170
ρ[f] [g cm^{-3}]	1.971 (173 K) 1.930 (298 K)	2.143 (100 K) 2.081 (298 K)	1.848 (100 K) 1.795 (298 K)	1.877 (173 K) 1.842 (298 K)	1.786 (173 K) 1.753 (298 K)
Δ_fH°[g] [kJ mol^{-1}]	932.1	625.5	647.7	789.8	941.9
Δ_fU°[h] [kJ kg^{-1}]	3697.1	1788.8	2327.0	2543.3	3050.0
EXPLO5 6.03 values:					
$-\Delta_{ex}H^{\circ}$[i] [kJ kg^{-1}]	6629	5398	5325	6384	5752
T_{det}	4645	3651	3536	4083	3843
P_{CJ}[j] [kbar]	456	343	361	418	358
V_{det}[k] [m s^{-1}]	10 142	8911	9519	9885	9472
V_0[l] [L kg^{-1}]	808	516	908	879	908

[a] Impact sensitivity (BAM drop-hammer (1 of 6)). [b] Friction sensitivity (BAM friction tester (1 of 6)). [c] Electrostatic discharge device (OZM research). [d] Oxygen balance ($\Omega=(xO-2yC-1/2zH)M/1600$). [e] Start of decomposition temperature from DSC/DTA ($\beta=5\,^{\circ}C$). [f] X-ray density; values for 298 K were recalculated from low temperature X-ray diffraction densities using the formula $\rho_{298K}=\rho_T/(1+\alpha_v(298-T)$,[11] $\alpha_v=1.5\cdot10^{-4}\,K^{-1}$. [g] Calculated enthalpy of formation. [h] Calculated energy of formation. [i] Heat of explosion. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of detonation gases (assuming only gaseous products).

cally. The 1-nitraminotetrazoles reach high heat of formations, the highest being 942 kJ mol^{-1} for compound **7**. All compounds are very powerful explosives and also very sensitive. The acids **1** and **2** even exploded during an attempt to gently pick crystals or to measure their sensitivities. Compound **2** was too sensitive for normal characterization. Looking toward their properties, 1-nitraminotetrazoles are typically primary explosives and most of them also detonate in the flame, like typical primaries.

Conclusions

1,1′-Dinitramino-5,5′-bitetrazole (**1**) was isolated and selected nitrogen-rich salts were synthesized. 1,1′-Dinitramino-5,5′-azobitetrazole (**2**) was synthesized for the first time by the nitration of 1,1′-diamino-5,5′-azobitetrazole and its potassium and ammonium salts were investigated. The synthesis of the 1-nitraminotetrazoles is carried out by nitration of 1-aminotetrazoles or 1-methoxycarbonyl protected 1-aminotetrazoles in dry acetonitrile using N_2O_5 as the nitrating reagent. All 1-nitraminotetrazoles are very powerful and sensitive explosives. They are exclusively in the sensitivity range of primary explosives. The detonation velocity values are calculated with the EXPLO5 V6.03 computer code and found to be all beyond the 9000 m s^{-1} mark for the CHNO compounds. The detonation pressures reach values beyond 300 kbar and culminate in 456 kbar for compound **1**. The aprotic potassium salts of the 1-nitraminotetrazoles decompose at higher temperatures than their salts with protic cations in general. The salts of **1** are more temperature-stable than the salts of **2**. The new compounds were characterized by low-temperature X-ray diffraction, NMR, IR, Raman spectroscopy, and investigated toward their physicochemical properties using DSC/DTA and BAM standard testing methods.

Experimental Section

General procedures

Raman spectra were recorded with a Bruker MultiRAM FT-Raman fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser ($\lambda=1064$ nm), IR spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSampl*IR* II ATR device. All spectra were recorded at ambient temperature; the samples were solids. NMR spectra were recorded at 25 °C with a JEOL Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^1H, 400.2 MHz; ^{13}C, 100.6 MHz), $MeNO_2$ (^{14}N, 40.7 MHz). Elemental analysis (C/H/N) were performed with a Elementar Vario EL analyzer. Decomposition points were either determined by differential scanning calorimetry (DSC) measurements with a Linseis DSC-PT10, using a heating rate of 5 °C min^{-1}, or DTA by using an OZM Research DTA 552-Ex instrument with Meavy 2.1.2 software. Sensitivity data (impact and friction) were performed using a drop-hammer and friction tester analogous to BAM (Bundesanstalt für Materialforschung und Prüfung).[12] The sensitivity toward electrostatic discharge was tested by using an OZM Research electric spark tester ESD 2010 EN.

CAUTION! All investigated compounds are potentially explosive energetic materials. This necessitates additional meticulous safety precautions (earthed equipment, Kevlar gloves, Kevlar sleeves, face shield, leather coat, and ear plugs).

1,1′-Dinitramino-5,5′-bitetrazole (1)

Compound **3** (522 mg, 1.56 mmol) was dissolved in 60 mL 2 M HCl and extracted six times with ethyl acetate (30 mL each). The combined organic phases were dried over magnesium sulfate and concentrated under reduced pressure without heating, yielding an orange oil. The orange oil was carefully dried under high vacuum, affording an ochre-colored residue, which was dissolved in a few mL diethyl ether and left to crystallize. Within a few hours, colorless single crystals, which were suitable for X-ray, were obtained in nearly quantitative yield.

DTA (5 °C min^{-1}): 107 °C (dec.); IR (atr): $\tilde{\nu}=3397$ (w), 3092 (m), 3031 (m), 2925 (m), 2854 (m), 2803 (m), 2613 (w), 1712 (w), 1625 (vs), 1460 (w), 1450 (w), 1398 (s), 1316 (s), 1290 (s), 1194 (s), 1116 (s), 1012 (m), 969 (m), 957 (m), 863 (s), 756 (s), 734 (s), 706 cm^{-1} (m); ^1H NMR ([D$_6$]DMSO, 25 °C): $\delta=5.67$ ppm; $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO, 25 °C): $\delta=140.5$ ppm; ^{14}N NMR ([D$_6$]DMSO, 25 °C): $\delta=-5.6$ ppm (N6); ^{15}N NMR ([D$_6$]DMSO, 25 °C): $\delta=3.9$ (N3), −5.6 (N6), −9.0 (N2), −49.2 (N4), −117.0 (N1), −122.0 ppm (N5); *m/z* (FAB$^-$): 257.2 [$C_2HN_{12}O_4^-$]; BAM drop-hammer: <1 J; friction tester: <5 N; ESD: 0.03 J.

Dipotassium 1,1′-dinitramino-5,5′-azobitetrazolate (4)

1,1′-diamino-5,5′-azobitetrazole[8] (490 mg, 2.5 mmol) was suspended in dry acetonitrile (50 mL). The mixture was cooled on ice and a solution of N_2O_5 (540 mg, 5 mmol) in cold acetonitrile (30 mL) was added dropwise. The diaminoazotetrazole dissolved and the red color of the product appeared. The reaction was quenched

with 7 mL of 2 M KOH. The red precipitate was filtered and dried in air. 550 mg (62%) of crystalline K_2DNAAzT was obtained.

DSC (5 °C min^{-1},°C): 180 °C (dec.). IR (atr): $\tilde{\nu}$ = 1635 (m), 1451 (s), 1434 (s), 1297 (s), 1242 (m), 1226 (w), 1119 (m), 1080 (vs), 1037 (s), 875 (w), 770 (w), 751 (w), 740 cm^{-1} (w). BAM drop-hammer: < 1 J; friction tester: < 5 N; ESD: < 2 mJ.

Diammonium 1,1′-dinitramino-5,5′-bitetrazolate (5)

Compound **3** (1.67 g, 5 mmol) was dissolved in HCl (80 mL, 4 M) and extracted four times with ethyl acetate (50 mL). An excess of 2 M NH_3 was added to the organic phase and the mixture was stirred vigorously for 10 min. The aqueous phase was separated and left for crystallization. Once the remaining liquid between the crystals was getting distinctly viscous a few mL of ice water was added and the crystals were isolated by filtration and washed with little ice water. 850 mg (58%) of **5** was isolated in the form of colorless, rhombic crystals.

DSC (5 °C min^{-1}): 210 °C (dec.); IR (atr): $\tilde{\nu}$ = 3187 (w), 3044 (w), 1406 (s), 1369 (m), 1277 (s), 1264 (vs), 1177 (w), 1166 (s), 1124 (m), 1032 (w), 1005 (w), 990 (w), 874 (s), 776 cm^{-1} (m); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3134 (2), 1613 (100), 1457 (6), 1279 (30), 1256 (7), 1154 (3), 1085 (19), 1016 (33), 988 (3), 892 (2), 747 (3), 730 (4), 519 (8), 323 cm^{-1} (3); ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.05 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 140.9 ppm; EA ($C_2H_8N_{14}O_4$, 292.18): calc.: C 8.22, H 2.76, N 67.11%; found: C 8.85, H 2.71, N 66.62%; *m/z* (FAB$^-$): 257 [$C_2HN_{12}O_4^-$]; BAM drop-hammer: 2 J; friction tester: < 5 N; ESD: 0.2 J.

Dihydroxylammonium 1,1′-dinitramino-5,5′-bitetrazolate (6)

Compound **3** (1.67 g, 5 mmol) was dissolved in HCl (80 mL, 4 M) and extracted four times with 50 mL ethyl acetate. Hydroxylamine (10 mmol, 50% aq.) in water (10 mL) was added and the mixture was stirred vigorously for 10 min. The aqueous phase was separated and left for crystallization. The crystals obtained were put on a filter paper and washed with a minimum amount of EtOH/Et_2O mixture. 939 mg (58%) colorless crystals were obtained.

DSC (5 °C min^{-1}): 155 °C (dec.); IR (atr): $\tilde{\nu}$ = 3073 (w), 2970 (w), 2706 (w), 1617 (w), 1539 (w), 1507 (w), 1369 (s), 1282 (vs), 1268 (s), 1158 (m), 1122 (s), 1011 (m), 870 (m), 816 (w), 778 (m), 723 (w), 712 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 3091 (2), 2993 (3), 1613 (100), 1588 (2), 1532 (2), 1460 (5), 1283 (24), 1254 (8), 1149 (7), 1096 (13), 1017 (25), 996 (3), 889 (2), 750 (3), 730 (3), 516 cm^{-1} (5); ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 10.02 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 141.0 ppm; EA ($C_2H_8N_{14}O_6$, 324.18): calc.: C 7.41, H 2.49, N 60.49%; found: C 8.14, H 2.47, N 60.54%; BAM drop-hammer: 2 J; friction tester: 5 N; ESD: 0.1 J.

Diammonium 1,1′-dinitramino-5,5′-azobitetrazolate (7)

Compound **4** (905 mg, 2.5 mmol) was dissolved in HCl (30 mL, 4 M) and extracted four times with ethyl acetate (25 mL). An excess of 2 M NH_3 was added to the organic phase and the mixture was stirred vigorously for 5 min. The aqueous phase was separated and left for crystallization. Once the remaining liquid between the crystals was turning distinctly viscous, a few mL of ice water was added and the crystals were isolated by filtration and washed with little ice water. 640 mg (80%) of **7** was isolated in the form of red crystals.

DSC (5 °C min^{-1}): 170 °C (dec.); IR (atr): $\tilde{\nu}$ = 3178 (m), 3067 (m), 2853 (w), 1394 (s), 1278 (vs), 1238 (s), 1222 (s), 1154 (w), 1094 (w), 1080 (w), 998 (w), 998 (w), 926 (w), 890 (w), 876 (m), 771 (m), 750 (m), 737 (m), 712 (w), 695 (w), 684 cm^{-1} (w); Raman (1064 nm, 200 mW, 25 °C): $\tilde{\nu}$ = 1490 (2), 1475 (19), 1453 (4), 1429 (100), 1398 (37), 1297 (2), 1244 (39), 1225 (11), 1157 (3), 1095 (30), 1082 (7), 1012 (12), 999 (7), 927 (19), 878 (8), 775 (3), 718 (2), 685 (2), 614 (2), 373 (2), 293 cm^{-1} (2); ^{1}H NMR ([D$_6$]DMSO, 25 °C): δ = 7.07 ppm; ^{13}C{^{1}H} NMR ([D$_6$]DMSO, 25 °C): δ = 157.97 ppm; EA ($C_2H_8N_{16}O_4$, 320.19): calc.: C 7.50, H 2.52, N 69.99%; found: C 9.03, H 2.67, N 69.97%; BAM drop-hammer: < 1 J; friction tester: < 5 N; ESD: 0.05 J.

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Keywords: energetic materials · nitramines · solid-state structure · tetrazoles

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FULL PAPER

Energetic Materials

D. Fischer, T. M. Klapötke, J. Stierstorfer, N. Szimhardt*

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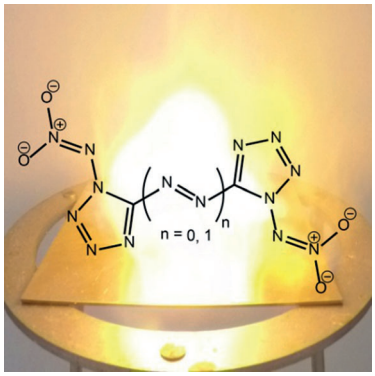
1,1′-Nitramino-5,5′-bitetrazoles



Dig for fire: 1-Nitraminobitetrazoles are a class of very high performance explosive materials with potential application as heavy-metal-free primary explosives. Now the corresponding 1-nitramino-azobitetrazoles, which are even more powerful but also more sensitive, have been synthesized.

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(54) **ENERGETIC ACTIVE COMPOSITION COMPRISING A DIHYDROXYLAMMONIUM SALT OR DIAMMONIUM SALT OF A BISTETRAZOLEDIOL**

(76) Inventors: **Thomas M. Klapötke**, München (DE); **Niko Fischer**, Augsburg (DE); **Dennis Fischer**, Augsburg (DE); **Davin G. Piercey**, Edmonton (CA); **Jörg Stierstorfer**, Wörthsee (DE); **Marius Reymann**, Erkheim (DE)

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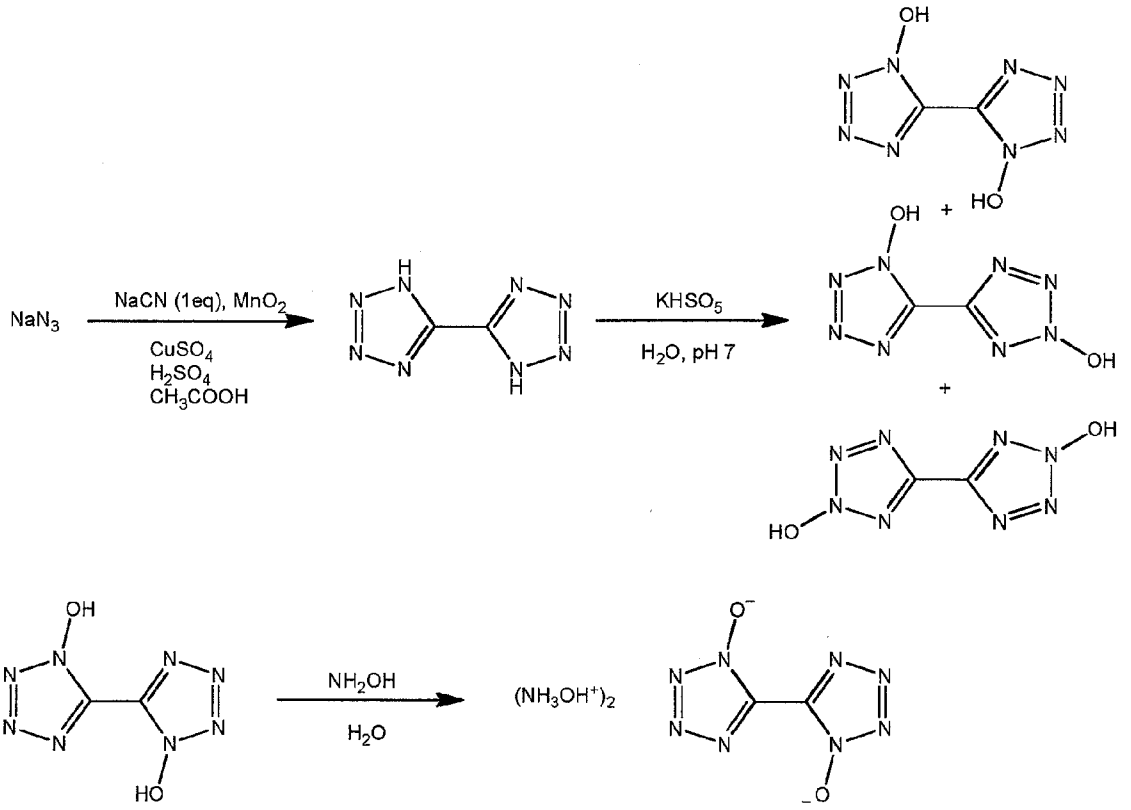
(57) **ABSTRACT**

The invention relates to an energetic active composition comprising a dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol or 5,5'-bistetrazole-2,2'-diol or a mixture of at least two of these salts.



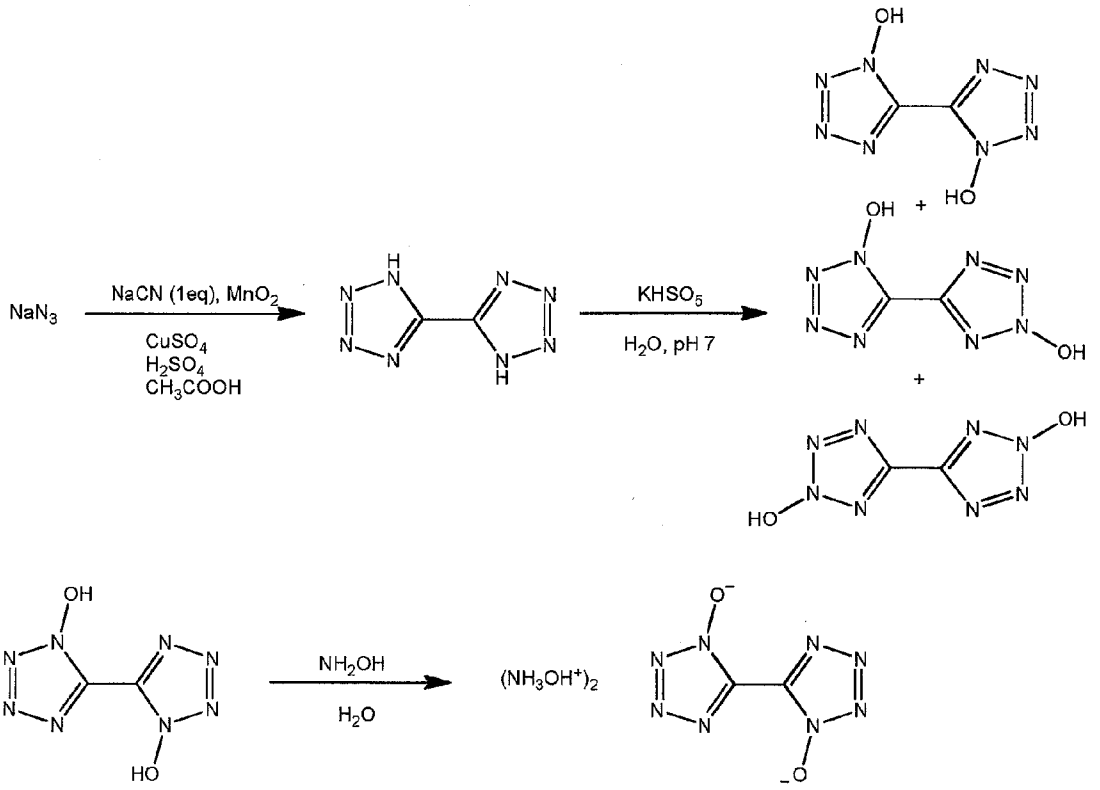

NaN3
NaCN (1eq), MnO2
CuSO4
H2SO4
CH3COOH
KHSO5
H2O, pH 7
NH2OH
H2O
(NH3OH+)2

Fig. 1

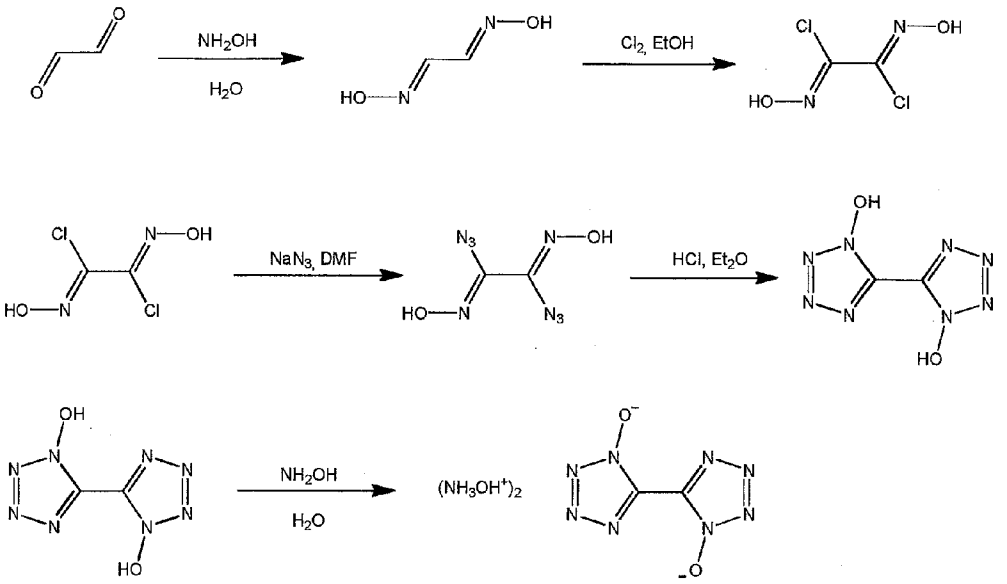


Fig. 2

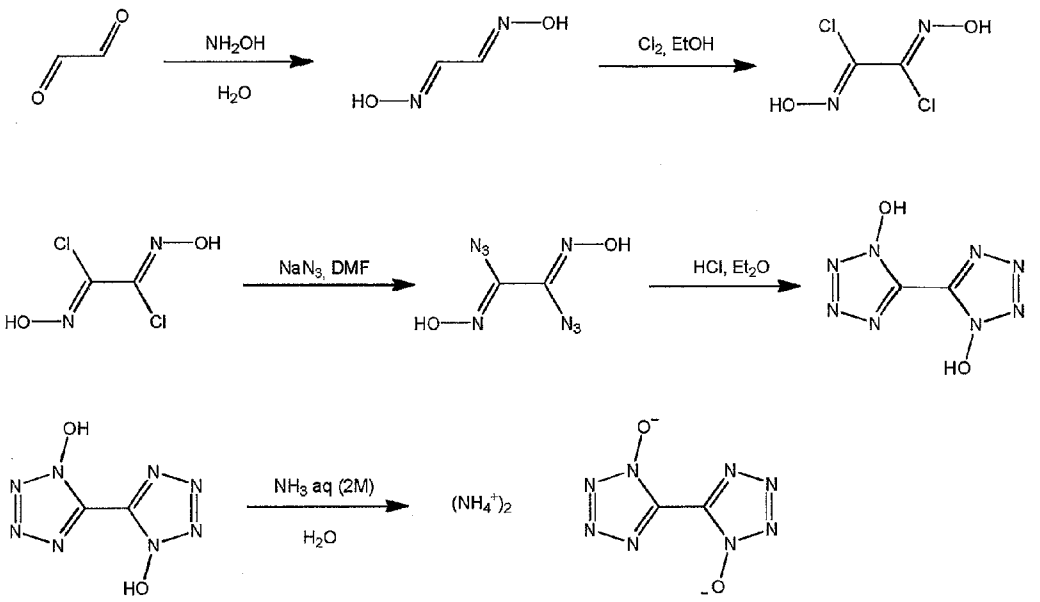


Fig. 3

ENERGETIC ACTIVE COMPOSITION COMPRISING A DIHYDROXYLAMMONIUM SALT OR DIAMMONIUM SALT OF A BISTETRAZOLEDIOL

[0001] The invention relates to an energetic active composition comprising a dihydroxylammonium salt or diammonium salt of a bistetrazolediol, to a use of the dihydroxylammonium salt or diammonium salt, to a process for preparing the dihydroxylammonium salt or diammonium salt, and to bistetrazolediols and also dihydroxylammonium salts and diammonium salts thereof.

[0002] U.S. Pat. No. 6,040,453 A discloses a process for preparing the diammonium salt of 5,5'-bi-1H-tetrazole using dicyan, sodium azide, ammonium chloride, and water as reaction medium. The process sees the dicyan added at low temperature to an aqueous solution comprising sodium azide and ammonium chloride. The mixture is subsequently heated. The 5,5'-bi-1H-tetrazole diammonium salt that is formed in this process is precipitated in the form of crystals that are of low solubility.

[0003] In Russian Journal of Organic Chemistry, volume 37, No. 3, 2001, pages 430 to 436, Tselinskii I. V. et al. disclose the synthesis and reactivity of aliphatic and aromatic carbohydroximoyl azides and of 5-substituted 1-hydroxytetrazoles based thereon.

[0004] Known from Göbel, M. et al., J. AM. CHEM. SOC. 2010, 132, pages 17216 to 17226 is the oxidation of nitrotetrazolate to give the nitrotetrazolate-2N-oxide anion, and the preparation of the hydroxylammonium salt thereof. In the theoretical calculation, the hydroxylammonium salt showed better detonation characteristics than the secondary explosive HMX. According to page 17224, left-hand column, second paragraph of the publication, however, the thermal stability of the salt and the extreme deliquescence of the free acid, which dissolves in absorbed water within a few minutes in air, likely rules out any practical application.

[0005] Additionally known as secondary explosives are nitramines, such as hexogen (RDX), octogen (HMX), or hexanitroisowurtzitane (CL-20), for example. One disadvantage of these nitramines and their reaction products after detonation lies in their toxicity and environmental impact. Additionally there is a need for more powerful secondary explosives. Such explosives are in fact already known, in the form of dinitroazofuroxane or octanitrocubane, for example. A disadvantage of these compounds lies in their sensitivity, which is high in comparison to other secondary explosives. Their synthesis, additionally, is very complex and requires 10 or more reaction steps.

[0006] It is an object of the present invention to provide an alternative energetic active composition which is easy to prepare and combines high powerfulness with safe handling and acceptable environmental impact. The intention additionally is to provide constituents of the active composition, a use of at least one constituent of this active composition, and a process for preparing such a constituent, and to specify compounds suitable as starting materials or intermediates for the production of such a constituent.

[0007] The object is achieved by means of the features of claims **1**, **2**, **3**, and **15** to **20**. Useful embodiments of the invention are evident from the features of claims **4** to **14**.

[0008] Provided in accordance with the invention is an energetic active composition which comprises a dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, or 5,5'-bistetrazole-2,2'-diol, or a mixture of at least two of these salts. An energetic active composition here refers to an active composition which reacts detonatively or deflagratively after its ignition. This composition may be an active pyrotechnic composition. An advantage of the stated dihydroxylammonium salts and diammonium salts is that the compounds in question are not nitramines and hence that no environmentally impactful nitrosamines are formed during their breakdown in the environment, either. The environmental compatibility of these salts is much better than the environmental compatibility of the stated nitramines and of the reaction products of the nitramines.

[0009] It has emerged, furthermore, that the dihydroxylammonium salt dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate, for example, has a calculated detonation velocity which is higher by 250 m/s than that of CL-20 and higher by 700 m/s than that of RDX. The diammonium salt diammonium 5,5'-bistetrazole-1,1'-diolate has a detonation velocity similar to that of RDX. Both salts therefore meet the preconditions required for a high-performance explosive. The detonation velocities were calculated using the program EXPLO5, version 5.05 (M. Sućeska, EXPLO5.04 program, Zagreb, Croatia, 2011; M. Sućeska, Calculation of detonation parameters by EXPLO5 computer program, *Materials Science Forum,* 2004, 465-466, 325-330; M. Sućeska, Calculation of the detonation properties of C—H—N—O explosives, *Propellants, Explos., Pyrotech.* 1991, 16, 197-202; M. Sućeska, Evaluation of detonation energy from EXPLO5 computer code results, *Propellants, Explos., Pyrotech.* 1999, 24, 280-285, M. L. Hobbs, M. R. Baer, *Proc. Of the* 10^{th} *Symp.* (*International*) *on Detonation,* ONR 33395-12, Boston, Mass., July 12-16, 1993, p. 409).

[0010] The sensitivity of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate and of diammonium 5,5'-bistetrazole-1,1'-diolate, additionally, is lower in each case than that of RDX. The impact sensitivity as determined by the drop hammer method is 7.5 J for RDX, meaning that RDX for use as secondary explosive has to be desensitized by addition of binders and plasticizers in order to be amenable to handling. Even without additives, in contrast, the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol (hereinafter: "TKX50") has a much lower impact sensitivity, of 20 J. Without additives, indeed, the diammonium salt of 5,5'-bistetrazole-1,1'-diol (hereinafter: "ABTOX") has an impact sensitivity of 35 J. Consequently TKX50 and ABTOX are much safer to handle than RDX, and permit easier compliance with the prescribed requirements for insensitive munitions.

[0011] The density of TKX50, furthermore, is higher than the density of RDX, and an active composition comprising TKX50 can have a much higher density than an active composition comprising RDX, owing to a low fraction of additives necessary for desensitization. This means that within a given volume it is possible to accommodate a higher mass of a TKX50-comprising active composition and so to achieve a higher performance than with RDX.

[0012] The density of ABTOX corresponds approximately to the density of RDX. ABTOX, furthermore, has an outstanding thermal stability. At a heating rate of 5° C./min, it decomposes only at a temperature of 290° C. and therefore far exceeds the decomposition temperature of RDX. ABTOX is therefore suitable for use at a high ambient temperature, at which RDX cannot be used.

[0013] The properties of TKX50 and ABTOX in comparison to 2,4,6-trinitrotoluene (2,4,6-TNT), RDX, β-HMX, and ϵ-CL-20 are set out in the table below:

	2,4,6-TNT	RDX	δ-HMX	ϵ-CL20	TKX50	ABTOX
Formula	$C_7H_5N_3O_6$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$	$C_2H_8N_{10}O_4$	$C_2H_8N_{10}O_2$
Molecular weight [g mol^{-1}]	227.1	222.1	296.2	438.2	236.2	204.2
IS [J][a]	15	7.5	7	4	20	35
FS [N][b]	353	120	112	48	120	360
ESD test [J][c]	—	0.2	0.2	—	0.1	0.25
N [%][d]	18.5	37.8	37.8	38.3	59.3	68.6
Ω [%][e]	−74.0	−21.6	−21.6	−11.0	−27.1	−47.0
$T_{dec.}$ [° C.][f]	290	210	285	195	221	290
Density [g cm^{-3}][g]	1.713	1.858	1.944	2.083	1.918	1.800
$\Delta_fU°$/kJ kg^{-1} [h]	−168	489	493	919	2006	1576
$\Delta_EU°$/kJ kg^{-1} [i]	5258	6190	6185	6406	6025	4195
T_E [K][j]	3663	4232	4185	4616	3954	2931
P_{C-J} [kbar][k]	235	380	415	467	424	316
D [m s^{-1}][l]	7459	8983	9221	9445	9698	8809
Gas volume [L kg^{-1}][m]	569	734	729	666	846	843

[a]Impact sensitivity (measured by the drop hammer method of the Bundesanstalt für Materialforschung und -prüfung, 1 of 6);
[b]friction sensitivity (measured with a friction apparatus according to the Bundesanstalt für Materialforschung und -prüfung, 1 of 6);
[c]measured with the electrostatic discharge device from the company OZM Research s.r.o., Czech Republic;
[d]nitrogen content;
[e]oxygen balance;
[f]decomposition temperature by DSC (Differential Scanning Calorimetry) measurement (5° C. per minute);
[g]determined by x-ray diffractometry at about 100 K;
[h] energy of formation, calculated by the CBS-4M method;
[i] explosion energy;
[j]explosion temperature;
[k]detonation pressure;
[l]detonation velocity;
[m]determined on the assumption of exclusively gaseous reaction products.

[0014] A further advantage of the salts encompassed by the active composition of the invention is that the final step in their synthesis can take place in an aqueous solution and as a result is relatively safe. From water or the aqueous solution, the salts crystallize in ideal blocklike crystals. These crystals are advantageous for the formulation of active compositions, since the low surface area/volume ratio of the blocks, relative to the needles which typically form with other explosive compounds, means that less plasticizer and binder are needed in order to provide an active substance amenable to safe handling. As a result, a higher content of explosive compound in the active composition, and hence a higher performance, are achieved. Moreover, the relatively low water-solubility of the salts is advantageous for their further processing.

[0015] In a test of the performance using the SSSRT (Small Scale Shock Reactivity Test), which examines the extent to which a block of aluminum buckles on detonation of an explosive under investigation, it was found that the performance of TKX50 following ignition thereof is similar to that of β-HMX and higher than that of RDX. The performance of ABTOX in the SSSRT was lower than that of RDX, owing to only partial detonation. The only partial detonation shows that ABTOX is very safe to handle, since its complete detonation requires a booster explosive.

[0016] Since it is known that explosive compounds which are less sensitive in the SSSRT require a greater amount in order to exhibit their performance, and more sensitive explosives with a relatively low performance exhibit an apparently higher performance, it can be assumed that the actual performances of TKX50 and ABTOX outstrip the performance of β-HMX.

[0017] The dihydroxylammonium salt of 5,5'-bistetrazole-2,2'-diol has a somewhat lower thermal stability than TKX50, but like TKX50, it has a relatively high density. The high density is a decisive criterion for powerful secondary explosives. The dihydroxylammonium salt of 5,5'-bistetrazole-2,2'-diol has a higher sensitivity than TKX50 and is therefore suitable not only as a secondary explosive but also as a booster explosive. A booster explosive is an explosive which serves to intensify the effect of another explosive, and whose sensitivity and amenability to initiation are lower by comparison with a primary explosive and higher by comparison with a secondary explosive.

[0018] That the stated dihydroxylammonium salts and diammonium salts would have such advantageous properties could not have been expected. According to Göbel, M. et al., J. AM. CHEM. SOC. 2010, 131, page 17224, left-hand column, second paragraph, the thermal stability and the extreme deliquescence of the free acid likely rule out any practical application. For the salt investigated in that publication, namely the hydroxylammonium salt of nitrotetrazolate 2N-oxide, the decomposition temperature was only 157° C. Given the fact that tests had shown anhydrous 5,5'-bistetrazole-1,1'-diol to be relatively unstable and to be almost impossible to handle safely as an explosive because of high sensitivity toward impact, friction, and electrostatic discharge, the skilled person could not have assumed that the dihydroxylammonium salts and diammonium salts encompassed by the active composition of the invention would have such outstanding qualities as explosives.

[0019] The invention further relates to the use of a dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, or 5,5'-bistetrazole-2,2'-diol or a mixture of at least two of these salts as explosive, more particularly as secondary explosive. The sensitivity of the dihydroxylammonium salt of 5,5'-bistetrazole-2,2'-diol has proved high enough to allow it to be used, indeed, as a booster explosive.

[0020] The invention additionally relates to a process for preparing a dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, or 5,5'-bistetrazole-2,2'-diol, or a mixture of at least two of these salts, with the following steps:

[0021] a) oxidizing 5,5'-bistetrazole to give a mixture of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, and 5,5'-bistetrazole-2,2'-diol, or

[0022] promoting the isomerization of diazidoglyoxime to 5,5'-bistetrazole-1,1'-diol or a 5,5'-bistetrazole-1,1'-diolate,

[0023] b) incubating the reaction product obtained according to step a) with hydroxylamine, hydroxylammonium ions, ammonium ions, or ammonia in aqueous solution, and

[0024] c) isolating the resultant precipitate.

[0025] The reaction product obtained according to step a) may be the mixture according to step a) or the 5,5'-bistetrazole-1,1'-diol. The oxidizing according to step a) may be accomplished by addition of $2KHSO_5.KHSO_4.K_2SO_4$ or of another inorganic or organic peroxo acid or hypofluorous acid, or another oxygen transfer agent, to the 5,5'-bistetrazole. $2KHSO_5.KHSO_4.K_2SO_4$ is sold under the trade name "Oxone" by the company DuPont. The addition of Oxone or of the other inorganic or organic peroxo acid or hypofluorous acid, or of the other oxygen transfer agent, takes place preferably in excess, in order to ensure complete oxidation of the 5,5'-bistetrazole. When Oxone is used in excess, the stated mixture is formed with a marked excess of 5,5'-bistetrazole-2,2'-diol. Oxidizing takes place preferably in an aqueous solution buffered to a pH of between 5 and 8, more particularly between 7 and 7.5. The buffering may be done, for example, using trisodium phosphate. At the stated pH, the 5,5'-bistetrazole is predominantly in deprotonated form. As a result, a nucleophilic attack by the 5,5'-bistetrazole on the peroxomonosulfate, which is necessary for oxidation by Oxone, is favored.

[0026] To increase the purity of the reaction product, the reaction product obtained in step a) by oxidizing of 5,5'-bistetrazole can be acidified and subsequently extracted with an organic extractant, more particularly ether. The ether stated here and hereinafter is more particularly diethyl ether. The reaction product may thereafter be obtained from the extract, more particularly by evaporation. To increase the purity further, the residue which remains after evaporation may be recrystallized. Methanol has proven a particularly suitable solvent for this purpose.

[0027] The dihydroxylammonium salt and the diammonium salt of 5,5'-bistetrazole-1,1'-diol have emerged as being markedly less soluble in water than are the dihydroxylammonium salts and diammonium salts of 5,5'-bistetrazole-1,2'-diol and 5,5'-bistetrazole-2,2'-diol. In order to precipitate specifically the dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol from the mixture formed by oxidizing, comprising 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, and 5,5'-bistetrazole-2,2'-diol, the different solubilities of the dihydroxylammonium salts and diammonium salts that can be precipitated from the mixture mean that it is necessary only to add the hydroxylamine or ammonia to the aqueous solution.

[0028] For precipitation of the dihydroxylammonium salts and diammonium salts of 5,5'-bistetrazole-1,2'-diol and 5,5'-bistetrazole-2,2'-diol, the aqueous solution, after the precipitation of the dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, more particularly with addition of further hydroxylamine or ammonia or of the hydroxylammonium ions or ammonium ions, can be concentrated by evaporation. By this means it is possible to exceed at least the solubility product of the dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,2'-diol or 5,5'-bistetrazole-2,2'-diol, and so the dihydroxylammonium salt or diammonium salt is precipitated. Alternatively the dihydroxylammonium salt or diammonium salt may be obtained from the residue resulting from the evaporation, by recrystallization, more particularly from an ethanol/water mixture.

[0029] Since oxidizing 5,5'-bistetrazole produces the 5,5'-bistetrazole-1,1'-diol in only a small amount in relation to the 5,5'-bistetrazole-2,2'-diol, it has emerged as being advantageous to promote the isomerization of diazidoglyoxime to bistetrazole-1,1'-diol, since in that case no 5,5'-bistetrazole-1,2'-diol and no 5,5'-bistetrazole-2,2'-diol is formed. The isomerization may be promoted by acylation, more particularly by means of acetyl chloride, or by incubation with gaseous HCl, more particularly in ether as solvent or in an ether-comprising solvent. The diazidoglyoxime can be produced by reaction of dichloroglyoxime with an azide, in which case there is a chlorine/azide exchange. The azide may be, for example, sodium azide. Dimethylformamide (DMF) may be used here as a solvent. The dichloroglyoxime may be produced by reaction of glyoxime with chlorine, in ethanol as solvent, for example. The glyoxime, in turn, may be produced by reaction of glyoxal with hydroxylamine.

[0030] In one advantageous embodiment of the process, the reaction of the dichloroglyoxime with the azide takes place in a nonaqueous solvent, more particularly dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP). The solvent with the resultant diazidoglyoxime is subsequently mixed with the ether and incubated with the gaseous HCl. The advantage of this process is that there is no need to isolate the diazidoglyoxime as an intermediate; instead, the glyoxime remains in solution. Since diazidoglyoxime is explosive, the preparation process is substantially safer as a result, and is also easier and more cost-effective to carry out, as a result of the dropping of an isolation step.

[0031] It is additionally possible, prior to step c), to evaporate the ether and the HCl and, where present, to evaporate the DMF. The evaporation of ether and HCl may possibly be facilitated by addition of H_2O, which then likewise requires evaporation. In the case of DMF as solvent, a mixture of dimethylammonium 5,5'-bistetrazole-1,1'-diolate and a 5,5'-bistetrazole-1,1'-diolate which comprises at least one counterion of the azide serving for the chlorine/azide exchange, and, in the case of NMP as solvent, a residue comprising 5,5'-bistetrazole-1,1'-diol, are obtained.

[0032] The stated mixture can be dissolved in H_2O, with subsequent addition of a hydroxylammonium salt, more particularly hydroxylammonium chloride, and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

[0033] The residue comprising 5,5'-bistetrazole-1,1'-diol may be taken up in an aqueous alkali hydroxide solution and the alkali 5,5'-bistetrazole-1,1'-diolate that precipitates may be isolated and dissolved in H_2O. It is possible subsequently for a hydroxylammonium salt, more particularly hydroxylammonium chloride, to be added, and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

[0034] Alternatively, in the above processes, instead of the hydroxylammonium salt, an ammonium salt, more particularly ammonium chloride, may also be added, and so the diammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

[0035] The invention additionally relates to 5,5'-bistetrazole-1,2'-diol and 5,5'-bistetrazole-2,2'-diol. Both compounds are each suitable as starting material or intermediate for producing the respective dihydroxylammonium salt or diammonium salt. The invention relates, furthermore, to the dihydroxylammonium salts and diammonium salts of 5,5'-bistetrazole-1,2'-diol and 5,5'-bistetrazole-2,2'-diol.

[0036] The invention is elucidated in more detail below by means of embodiments. In the figures:

[0037] FIG. **1** shows a reaction scheme of a first synthesis process for producing the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol,

[0038] FIG. **2** shows a reaction scheme of a second synthesis process for producing the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol, and

[0039] FIG. **3** shows a reaction scheme of a synthesis process for producing the diammonium salt of 5,5'-bistetrazole-1,1'-diol.

[0040] To carry out the first process, for the synthesis of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate according to FIG. **1**, the following procedure may be adopted:

[0041] 3.0 g of 5,5'-bistetrazole (21.7 mmol) are dissolved in 200 ml of water. 80.0 g of Oxone (109 mmol, 5 eq) are added to the resulting clear solution, and the resultant solution is buffered to a pH of 7 using trisodium phosphate. The mixture is stirred at room temperature for 5 hours and then acidifed with concentrated sulfuric acid. The reaction product is extracted using ether. Evaporation of the ether gives the crude product as a pale yellow solid. The solid is dissolved in methanol and recrystallized therefrom in order to remove remaining sulfates or phosphates from it. The reaction produces a mixture of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-2,2'-diol, and 5,5'-bistetrazole-1,2'-diol in a total yield of 71% (2.60 g, 15.3 mmol). In this mixture the 2,2' isomer is the principal product.

[0042] 1.7 g of the isomer mixture (10 mmol) are dissolved in 20 ml of hot water. An aqueous solution of 50% (w/w) hydroxylamine (1.23 g, 20 mmol) is added to the solution. A colorless precipitate is formed immediately. The precipitate is dissolved again by heating of the mixture. In the course of slow cooling, the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is precipitated. The salt is isolated by filtration. The salt is then dissolved in water and recrystallized therefrom in order to remove remaining 1,2' isomer and 2,2' isomer, both of which have a better solubility in water than does the 1,1' isomer.

[0043] The diammonium salt of 5,5'-bistetrazole-1,1'-diol may be obtained in an analogous way from the isomer mixture in solution in water. For this purpose, gaseous ammonia is introduced into the aqueous solution or an aqueous ammonia solution is added to the aqueous solution. A precipitate forms immediately, and is dissolved again by heating of the mixture. In the course of slow cooling, the diammonium salt of 5,5'-bistetrazole-1,1'-diol is precipitated. The salt is isolated by filtration and then dissolved in water and recrystallized therefrom, in order to remove remaining 1,2' isomer and 2,2' isomer, both of which have a better solubility in water than does the 1,1' isomer.

[0044] Owing to the predominant formation of the 2,2' isomer during the oxidation of the 5,5'-bistetrazole, the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol can be obtained in the above process only in a relatively low yield of 13% (0.31 g, 1.3 mmol). In order to obtain a higher yield, the synthesis may be carried out in accordance with the reaction scheme shown in FIG. **2**. For this purpose, dichloroglyoxime is synthesized first of all, and 5,5'-bistetrazole-1,1'-diol in dihydrate form is prepared therefrom, as described in Tselinskii, I. V. et al., Russian Journal of Organic Chemistry, volume 37, No. 3, 2001, pages 430 to 436. 2.06 g (10 mmol) of the resulting dihydrate are dissolved in 50 ml of hot water. A 50% strength (w/w) hydroxylamine solution (1.32 g, 20 mmol) is added to it. On cooling of the solution to room temperature, the dihydroxylammonium salt precipitates in the form of crystals. It is isolated by filtration and dried in air. The yield is 82%.

[0045] The procedure adopted for preparing the dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-2,2'-diol is as for the synthesis according to FIG. **1**. After the precipitation of the dihydroxylammonium salt or diammonium salt of the 1,1' isomer on cooling of the mixture, the dihydroxylammonium salt or diammonium salt of 5,5'bistetrazole-2,2'-diol can be obtained by evaporating the solvent and recrystallizing the resultant residue from an ethanol/water mixture.

[0046] The synthesis of the diammonium salt of 5,5'-bistetrazole-1,1'-diol may also be carried out in accordance with the reaction scheme shown in FIG. **3**. For this purpose, dichloroglyoxime is first of all synthesized and 5,5'-bistetrazole-1,1'-diol in dihydrate form is prepared from it as described in Tselinskii, I. V. et al., Russian Journal of Organic Chemistry, volume 37, No. 3, 2001, pages 430 to 436. 2.06 g (10 mmol) of the resulting dihydrate are suspended in 10 ml of a 2 M aqueous ammonia solution. Following addition of 90 ml of water, the mixture is heated to its boiling point. A clear solution is formed. On cooling of the solution to room temperature, the diammonium salt precipitates in the form of crystals. It is isolated by filtration and dried in air. The yield is 1.14 g (5.57 mmol, 56%).

[0047] Further Synthesis Processes:

[0048] TKX50: Dichloroglyoxime (785 mg, 5 mmol) is dissolved at room temperature in 10 ml of N,N'-dimethylformamide (DMF). The solution is cooled to 0° C. and NaN_3 (715 mg, 11 mmol) is added. The mixture is stirred at 0° C. for 40 minutes, during which NaCl precipitates and diazidoglyoxime remains in solution. The mixture is transferred to a flask in which 100 ml of diethyl ether at 0° C. have been placed, and HCl gas is introduced, the flask being cooled continually in a salt/ice bath and the temperature being not to exceed 20° C. When the temperature falls back to 0-5° C. in spite of further introduction of gas, HCl saturation of the ether phase is achieved. A precipitate which forms on introduction of HCl first undergoes agglomeration and, as HCl saturation increases, is resuspended. The flask is sealed tightly with a stopper, and stirring of the mixture is continued overnight at room temperature under a slight HCl overpressure, which

forms in the flask as a result of warming to room temperature. The pressure is let off and the mixture is transferred to an open vessel, allowing diethyl ether and HCl to evaporate either overnight at room temperature or in 1-2 h at 50° C. When the major part of the ether has evaporated, 50 ml of water are added, and a clear solution is formed. The water is removed on a rotary evaporator and the DMF that is left is stripped off under a high vacuum, producing a mixture of dimethylammonium 5,5'-bistetrazole-1,1'-diolate and disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate in the form of a colorless solid. The solid is dissolved in the minimum volume of boiling water (about 10 ml) and hydroxylammonium chloride (750 mg, 10.8 mmol, 2.16 eq) is added in the form of a concentrated aqueous solution. TKX50 precipitates from the solution in a yield of 74.6% (882 mg, 3.73 mmol). It can be filtered off with suction, washed with a little cold water, and dried in the air.

[0049] ABTOX: The synthesis procedure follows the same lines as the synthesis procedure for TKX50, until the mixture of dimethylammonium 5,5'-bistetrazole-1,1'-diolate and disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate is obtained. It is again dissolved in the minimum volume of boiling water (about 10 ml), and ammonium chloride (800 mg, 15.0 mmol, 3 eq) is added in the form of a concentrated aqueous solution. In the case of ABTOX it is necessary to add a somewhat greater excess of ammonium salt, since the water-solubility of ABTOX is somewhat greater than that of TKX50. It is also necessary to reduce the volume of the solution comprising ABTOX and dimethylammonium chloride by about 30% on a rotary evaporator in order to precipitate ABTOX. It can be isolated in a yield of 78.3% (799 mg, 3.91 mmol). Similarly to TKX50, ABTOX is filtered off with suction, washed with a little cold water, and dried in the air.

[0050] TKX50: Dichloroglyoxime (785 mg, 5 mmol) is dissolved at room temperature in 10 ml of N-methyl-2-pyrrolidone (NMP). The solution is cooled to 0° C. and NaN_3 (715 mg, 11 mmol) is added. The mixture is stirred for 40 minutes at 0° C. NaCl is precipitated, and diazidoglyoxime remains in solution. The mixture is transferred to a flask in which 150 ml of diethyl ether have been placed, and the mixture is cooled to 0° C. in a salt/ice bath. HCl gas is introduced into the mixture, during which the temperature is not to exceed 20° C. Saturation of the ether with HCl is achieved as soon as the temperature drops to 0-5° C. again in spite of continuing introduction of HCl. A thick precipitate which has formed at the beginning of gas introduction is rapidly resuspended when HCl saturation is achieved. The flask is sealed tightly and stirring of the mixture is continued overnight at room temperature under a slight HCl overpressure, which has become established in the flask as a result of the warming to room temperature. The pressure is let off and the mixture is transferred to an open vessel, where diethyl ether and HCl can evaporate overnight at room temperature or in 1-2 h at 50° C. When the major part of the diethyl ether has evaporated, 50 ml of water are added and the solvent is removed again on a rotary evaporator. The viscous residue, which contains 5,5'-bistetrazole-1,1'-diol, NaCl, and NMP, is taken up in 20 ml of 2M NaOH, and the disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate begins to precipitate. The mixture is boiled briefly and, on cooling, there is virtually complete precipitation of the disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate. This product is filtered off with suction and dissolved in the minimum volume of boiling water (about 10 ml). Hydroxylammonium chloride (750 mg, 10.8 mmol, 2.16 eq) is added in the form of a concentrated aqueous solution. TKX50 precipitates from the solution in a yield of 85.1% (1.00 g, 4.25 mmol). It is filtered off with suction, washed with cold water, and dried in the air.

[0051] ABTOX: The synthesis procedure follows the same lines as the synthesis procedure for TKX50, until the disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate is obtained. It is again dissolved in the minimum volume of boiling water (about 10 ml), and ammonium chloride (800 mg, 15.0 mmol, 3 eq) is added in the form of a concentrated aqueous solution. In the case of ABTOX it is necessary to add a somewhat greater excess of ammonium salt, since the water-solubility of ABTOX is somewhat greater than that of TKX50. It is also necessary to reduce the volume of the solution comprising ABTOX and NaCl by about 30% on a rotary evaporator in order to precipitate ABTOX. It can be isolated in a yield of 81.3% (830 mg, 4.07 mmol). Similarly to TKX50, ABTOX is filtered off with suction, washed with a little cold water, and dried in the air.

[0052] The advantages of the further synthesis processes of TKX50 and ABTOX lie primarily in avoidance of the isolation of the diazidoglyoxime intermediate, which is highly sensitive to impact and friction. The high-sensitivity intermediate remains in solution throughout the operation, and so there are no objective dangers during the synthesis. The dimethylammonium 5,5'-bistetrazole-1,1'-diolate and disodium 5,5'-bistetrazole-1,1'-diolate tetrahydrate intermediates that are isolated here display no substantial impact sensitivity (both >40 J) and also no substantial friction sensitivity (both >360 N). A further advantage of the synthesis presented here is the saving of two reaction steps, namely the isolation of diazidoglyoxime and 5,5'-bistetrazole-1,1'-diol dihydrate, which ties in well with an industrial-scale preparation of TKX50 and ABTOX not only on financial grounds.

1-20. (canceled)

21. An energetic active composition comprising a dihydroxylammonium salt or diammonium salt of 5,5' -bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, or 5,5'-bistetrazole-2,2'-diol, or a mixture of at least two of these salts.

22. A process for preparing a dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, or 5,5'-bistetrazole-2,2'-diol, or a mixture of at least two of these salts, with the following steps:

a) oxidizing 5,5'-bistetrazole to give a mixture of 5,5'-bistetrazole-1,1'-diol, 5,5'-bistetrazole-1,2'-diol, and 5,5'-bistetrazole-2,2'-diol, or promoting the isomerization of diazidoglyoxime to 5,5'-bistetrazole-1,1'-diol or a 5,5'-bistetra-zole-1,1'-diolate,

b) incubating the reaction product obtained according to step a) with hydroxylamine, hydroxylammonium ions, ammonium ions, or ammonia in aqueous solution, and

c) isolating the resultant precipitate.

23. The process as claimed in claim **22**, wherein the oxidizing according to step a) takes place by addition of $2KHSO_5.KHSO_4.K_2SO_4$ or of another inorganic or organic peroxo acid or hypofluorous acid or another oxygen transfer agent to the 5,5'-bistetrazole.

24. The process as claimed in claim **22**, wherein the oxidizing takes place in an aqueous solution buffered to a pH of between 5 and 8.

25. The process as claimed in claim **22**, wherein the reaction product obtained in step a) by oxidizing of 5,5'-bistetrazole is acidified and subsequently extracted with an organic

extractant and thereafter recovered from the extract the reaction product being subsequently optionally recrystallized.

26. The process as claimed in claim **22**, wherein, in step a), 5,5'-bistetrazole is oxidized and the aqueous solution, after the precipitation of the dihydroxylammonium salt or diammonium salt of 5,5'-bistetrazole-1,1'-diol is concentrated by evaporation, where either as a result at least the solubility product of the dihydroxyammonium salt or diammonium salt of 5,5'-bistetrazole-1,2'-diol or 5,5'-bistetrazole-2,2'-diol is exceeded, and so the dihydroxylammonium salt or diammonium salt precipitates, or the dihydroxylammonium salt or diammonium salt is obtained from the residue resulting from the evaporation by recrystallization.

27. The process as claimed in claim **22**, wherein the promoting of the isomerization takes place by acylation or by incubation with gaseous HCl.

28. The process as claimed in claim **22**, wherein the diazidoglyoxime is produced by reaction of dichloroglyoxime with an azide.

29. The process as claimed in claim **27**, wherein the diazidoglyoxime is produced by reaction of dichloroglyoxime with an azide.

30. The process as claimed in claim **28**, wherein the reaction of the dichloroglyoxime with the azide takes place in a nonaqueous solvent, the solvent with the resultant diazidoglyoxime being subsequently mixed with the ether and incubated with the gaseous HCl.

31. The process as claimed in claim **29**, wherein the reaction of the dichloroglyoxime with the azide takes place in a nonaqueous solvent, the solvent with the resultant diazidoglyoxime being subsequently mixed with the ether and incubated with the gaseous HCl.

32. The process as claimed in claim **30**, wherein before step c) the ether and the HCl are evaporated off and, where present, dimethylformamide (DMF) is evaporated off, and so, in the case of DMF as solvent, a mixture of dimethylammonium 5,5'-bistetrazole-1,1'-diolate and a 5,5'-bistetrazole-1,1'-diolate which comprises at least one counterion of the azide, and in the case of N-methyl-2-pyrrolidone (NMP) as solvent a residue comprising 5,5'-bistetrazole-1,1'-diol, is obtained.

33. The process as claimed in claim **31**, wherein before step c) the ether and the HCl are evaporated off and, where present, dimethylformamide (DMF) is evaporated off, and so, in the case of DMF as solvent, a mixture of dimethylammonium 5,5'-bistetrazole-1,1'-diolate and a 5,5'-bistetrazole-1,1'-diolate which comprises at least one counterion of the azide, and in the case of N-methyl-2-pyrrolidone (NMP) as solvent a residue comprising 5,5'-bistetrazole-1,1'-diol, is obtained.

34. The process as claimed in claim **32**, wherein the dimethylammonium 5,5'-bistetrazole-1,1'-diolate is dissolved in H_2O and subsequently a hydroxylammonium salt is added, and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

35. The process as claimed in claim **33**, wherein the dimethylammonium 5,5'-bistetrazole-1,1'-diolate is dissolved in H_2O and subsequently a hydroxylammonium salt is added, and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

36. The process as claimed in claim **32**, wherein the residue comprising 5,5'-bistetrazole-1,1'-diol is taken up in an aqueous alkali hydroxide solution and the precipitating alkali 5,5'-bistetrazole-1,1'-diolate is isolated and dissolved in H_2O, with subsequent addition of a hydroxylammonium salt and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

37. The process as claimed in claim **33**, wherein the residue comprising 5,5'-bistetrazole-1,1'-diol is taken up in an aqueous alkali hydroxide solution and the precipitating alkali 5,5'-bistetrazole-1,1'-diolate is isolated and dissolved in H_2O, with subsequent addition of a hydroxylammonium salt and so the dihydroxylammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

38. The process as claimed in claim **34**, wherein an ammonium salt is added instead of the hydroxylammonium salt, and so the diammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

39. The process as claimed in claim **35**, wherein an ammonium salt is added instead of the hydroxylammonium salt, and so the diammonium salt of 5,5'-bistetrazole-1,1'-diol is obtained as the precipitate.

40. 5,5'-Bistetrazolediol or salt thereof, wherein the 5,5'-Bistetrazolediol is 5,5'-Bistetrazole-1,2'-diol or 5,5'-Bistetrazole-2,2'-diol and the salt is dihydroxylammonium salt or diammonium salt.

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Bis(3,4,5-trinitropyrazolyl)methane and bis(3,5-dinitro-4-aminopyrazolyl)methane

The invention relates to bis(3,4,5-trinitropyrazolyl)methane (UMX1 or BTNPM) and its source product bis(3,5-dinitro-4-aminopyrazolyl)methane (UMX2 or BDNAPM), to an energetic active mass comprising these substances, to a use of these substances as well as to methods for synthesizing these substances. The lack of high-performing secondary explosives with both adequate performance and high oxygen content which explosives have a good thermal stability and can be synthesized in a feasible way is known. In explosive formulations a binder is usually used to improve the processing properties of the formulation. The binder in such formulations is usually a material which decreases the oxygen balance significantly. If an oxygen rich explosive is used in the formulation the oxygen balance can be kept at an acceptable level without having "underoxidized" detonation products like methane, ethylene, HCN and so forth. With all the carbon and hydrogen content in the formulation being oxidized to water and carbon monoxide, an optimum performance can be achieved.

Known secondary explosives are hexogen (RDX), octogen (HMX), hexanitrohexaazaisowurtzitane (CL-20) and nitropenta (PETN).

From Yin, P. et al., Chem. Eur. J., 2014, 20, pages 16529 to 16536 N,N'-ethylene-bridged 4,4'-diaminobis(pyrazole) and its derivatives are known. The density and detonation velocity of these substances is not particularly high.

From Claramunt, R. M. et al., Bulletin de la Société Chimique de France, 1983, No. 1-2, pages II-5 to II-10, methylene-1,1'-dipyrazole derivatives having amino or nitro substituents are known.

From DE 38 20 739 A1 metal salts of halogen substituted pyrazoles are known.

From Dalinger, I. L. et al., Synthesis, 2012, 44, pages 2058 to 2064 4-chloro-3,5-dinitropyrazole and the formation of a salt thereof is known.

From WO 96/20146 the use of pyrazole derivatives with hydrophobic groups as nitrification inhibitors is known. One of the derivatives is a substituted bispyrazolylmethane.

The problem to be solved by the present invention is to provide alternative energetic substances, an energetic active mass comprising at least one of these substances, a use of at least one of these substances and methods for synthesizing these substances.

The problem is solved by the subject-matter of claims 1 to 3, 5, 6 and 11. Embodiments of the invention are subject-matter of claims 4, 7 to 10, 12 and 13.

According to the invention bis(3,4,5-trinitropyrazolyl)methane (UMX1, BTNPM) and bis(3,5-dinitro-4-aminopyrazolyl)methane (UMX2, BDNAPM) are provided. Both substances have been found to be high performing explosives. Furthermore, an energetic active mass comprising UMX1, UMX2 or a mixture thereof and a use of UMX1, UMX2 or a mixture thereof are provided according to the invention.

An energetic active mass according to the invention is an active mass that deflagrates or explodes after its ignition. The active mass may be a pyrotechnic active mass. The energetic active mass according to the invention can comprise or consist of a mixture of UMX1 and a powdered metal, such as aluminum or magnesium. The mixing of UMX1 with the powdered metal, in particular aluminum, results in an exceedingly high explosion energy and therewith a high impulse upon detonation. This feature in combination with the high performance of the substance as such is unique. The high impulse upon detonation is particularly useful in ammunition for torpedoes.

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The detonation velocity of UMX1 is higher than that of PETN, RDX or HMX. Also the density of UMX1 is higher than that of PETN, RDX or HMX. The calculation of the detonation velocity as well as the energy of explosion was performed by use of the program EXPLO5, Version 6.02 (M. Sućeska, EXPLO5 V6.02 program, *Brodarski Institute,* Zagreb, Croatia, 2014; M. Sućeska, Calculation of detonation parameters by EXPLO5 computer program, *Materials Science Forum*, 2004, 465-466, 325-330; M. Sućeska, Calculation of the detonation properties of C-H-N-O explosives, *Propellants, Explos., Pyrotech.* 1991, *16*, 197-202; M. Sućeska, Evaluation of detonation energy from EXPLO5 computer code results, *Propellants, Explos., Pyrotech.* 1999, *24*, 280-285; M. L. Hobbs, M. R. Baer, *Proc. of the 10th Symp. (International) on Detonation,* ONR 33395-12, Boston, MA, July 12–16, 1993, p. 409).

The features of UMX1 and UMX2 compared to PETN, RDX, β-HMX and ε-CL-20 are shown in the following table:

	PETN	RDX	HMX	CL-20	UMX1	UMX2	85% w/w UMX1 + 15% w/w Al
Formula	$C_5H_8N_4O_{12}$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$	$C_6H_6N_{12}O_{12}$	$C_7H_2N_{10}O_{12}$	$C_7H_6N_{10}O_8$	
MW [g mol^{-1}]	316.1	222.12	296.16	438.2	418.15	358.19	
IS [J] [a]	4	7.5	7	4	4	11	
FS [N] [b]	80	120	112	48	144	>360	
ESD-test [J] [c]	0.1	0.2	0.2	-	0.1	>1.5	
N [% w/w] [d]	17.72	37.8	37.8	38.3	33.50	39.10	
Ω [% w/w] [e]	-10.12	-21.61	-21.61	-11.0	-11.48	-40.20	-23.1
$T_{dec.}$ [°C] [f]	150	210	285	195	205	310	
Density [g cm^{-3}] [g]	1.778	1.80	1.905	2.038	1.934	1.802	2.02
$\Delta_f U°$ [kJ kg^{-1}] [h]	-1611	415,6	353.0	982	976.8	655.8	
$-\Delta_E U°$ [kJ kg^{-1}] [i]	6190	5843	5794	6473	6254	5052	8003
T_E [K] [j]	4306	3814	3687	4654	4570	3580	5527
p_{CJ} [kbar] [k]	320	342	389	446	393	295	360
D [m s^{-1}] [l]	8320	8838	9235	9342	9300	8372	8583
Gas vol. [L kg^{-1}] [m]	688	786	767	669	704	706	524
SSRT [mg SiO_2] [n]		858	971		895	726	

[a] impact sensitivity (BAM drophammer method, value of a given drop energy if the result of at least one of six tests was positive for that drop energy); [b] friction sensitivity (BAM friction tester, value of a given friction force if the result of at least one of six tests was positive for that friction force); [c] OZM electrostatic discharge device ; [d] nitrogen content; [e] oxygen balance; [f] decomposition temperature from DSC (measured at a heating rate of 5 °C min^{-1}); [g] values calculated for a temperature of 298 K based on X-ray diffraction measurements; [h] calculated (CBS-4M) energy of formation; [i] energy of explosion; [j] explosion temperature; [k] detonation pressure; [l] detonation velocity; [m] assuming only gaseous products; [n] dent size measured by filling the dent with powdered SiO_2 and measuring the resulting weight.

For the calculation of the energy of formation according to the table the enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. For the calculation of the energies of formation according to the table the modified CBS-4M method (M referring to the use of minimal population localization) was applied. The CBS-4M method is a re-parameterized version of the original CBS-4 method and also includes some additional empirical corrections.

DSC measurements at a heating rate of 5 °C/min revealed that UMX1 is thermally stable up to 205 °C. Based on X-ray diffraction measurements the density of the material was calculated to be 1.934 g/cm^3 for a temperature of 298 K. This density provides the material with a good energetic performance. The oxygen balance of UMX 1 is −11.48% w/w.

"85% w/w UMX1 + 15% w/w Al" means a mixture of 85% w/w of a powder of UMX1 and 15% w/w of an aluminum powder. Very remarkable is the high energy of explosion of this mixture which energy of explosion is above 8000 kJ/kg. In the "small scale shock reactivity test" (SSRT) UMX2 and UMX1 showed good results. In this test a defined amount of explosive is tamped within a steel housing and is exploded against an aluminum block followed by measuring the volume of the resulting dent by filling this dent with powdered SiO_2 and measuring the resulting weight. The SSRT measures the shock reactivity (explosiveness) of energetic materials. The corresponding result obtained with hexanitrostilbene (HNS) was only 703 mg SiO_2.

UMX1 can be obtained by the oxidation of its precursor UMX2. UMX2 has interesting properties as a thermally stable insensitive explosive. The compound is stable up to 310 °C and has a calculated detonation velocity of 8372 m/s and a detonation pressure of 295 kbar while having low sensitivity values of 11 J towards impact and more than 360 N towards friction. The combination of these values makes the compound unique. A comparison with the common used HNS (hexanitrostilbene) shows that it has a decomposition point which is higher by 10 °C but HNS is the inferior performing explosive.

UMX1 can be synthesized in a five step procedure from commercially available pyrazole as shown in Fig. 1. The synthesis of substances 1 to 4 according to Fig. 1 is disclosed in Yin, P. et al., Chem. Eur. J., 2014, 20, pages 16529 to 16536.

UMX2 can be synthesized from 3,5-dinitro-4-aminopyrazolate anions by contacting these anions with a methylene bridge inducing agent in a solution comprising or consisting of a polar solvent. The 3,5-dinitro-4-aminopyrazolate anion can be provided as an ammonium or any alkali or alkaline earth salt, e. g. a sodium salt, of 3,5-dinitro-4-aminopyrazole. The methylene bridge inducing agent may be diiodomethane (CH_2I_2). The solvent may be an aprotic solvent, in particular dimethylformamide. The methylene bridge inducing effect of CH_2I_2 in a solution consisting of dimethylformamide is known in the art, e. g. from Pampaloni, G., et al., Organometallics, 2007, 26(17), pages 4278 to 4286. The 3,5-dinitro-4-aminopyrazolate anions may be contacted with said methylene bridge inducing agent at a temperature of at least 50 °C, in particular at least 60 °C, in particular at least 70 °C, in particular at least 80 °C. The UMX2 can be obtained from the solution by precipitation by reducing polarity in the solution, in particular by addition of water to the solution.

UMX1 can be obtained from UMX2 by oxidation of UMX2. For this purpose H_2O_2, H_2SO_4 or a mixture of H_2O_2 and H_2SO_4 can be used as a means for oxidation and as a solvent for said UMX1 and said UMX2. The UMX1 can be obtained from a

solution comprising or consisting of the solvent and UMX1 by precipitation by addition of water to the solution.

Embodiments of the invention:

A) Synthesis of UMX2

The sodium salt of 3,5-dinitro-4-aminopyrazole can be easily obtained by neutralization of 3,5-dinitro-4-aminopyrazole or by reacting the ammonium salt of it with sodium hydroxide in ethanol or water. In the latter case the formed ammonia is volatile. The sodium salt can be easily recrystallized from water to get a highly pure sample. 4.29 g (22 mmol) sodium 3,5-dinitro-4-aminopyrazolate were suspended in 15 mL DMF and 805 µl (2.68 g, 10 mmol) diiodomethane was added. The mixture was stirred at 90 °C overnight for 16 h and poured on 100 mL of water. A little dilute sodium thiosulfate solution is added to reduce the precipitated iodine (from side reactions) until the suspension gives a nice and clean yellow color. The precipitated product was filtered and washed with water and dried in air to give 3.18 g UMX2 (yield: 89 % mol/mol) as yellow solid.

The features of the products are as follows:

DSC (5 °C min^{-1}, °C): 310°C (dec.); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 3484 (w), 3462 (w), 3368 (w), 3349 (w), 1642 (s), 1579 (w), 1508 (m), 1477 (s), 1445 (m), 1386 (m), 1352 (w), 1300 (s), 1274 (vs), 1234 (m), 1218 (m), 1150 (w), 1103 (w), 1063 (w), 1004 (m), 886 (w), 827 (m), 803 (w), 785 (m), 759 (m), 743 (w), 736 (w); **Raman** (1064 nm, 10 mW, 25 °C, cm−1): $\tilde{\nu}$ = 3352 (3), 3032 (2), 1639 (22), 1568 (8), 1471 (8), 1446 (5), 1407 (7), 1391 (27), 1375 (100), 1352 (39), 1316 (4), 1294 (4), 1274 (6), 1238 (10), 1209 (2), 1151 (2), 1007 (6), 834 (46), 802 (6), 792 (12), 740 (11), 676 (2), 638 (5), 358 (9), 226 (2); **^{1}H NMR** (400 MHz, DMSO-*d_6*, 25 °C, ppm): δ=7.29, 7.16; **^{13}C NMR{^{1}H}** (400 MHz, DMSO-*d_6*, 25 °C, ppm) δ=142.1, 131.7, 130.9, 67.2; **m/z (DEI^{+})**: 358.2 [M^{+}]; **EA** ($C_7H_6N_{10}O_8$, 258.19) calc.: C 23.47,

H 1.69, N 39.10 % w/w; found: C 23.73, H 1.81, N 38.90 % w/w; **BAM drop-hammer**: 11 J (<100 µm); **friction tester**: > 360 N (<100 µm); ESD > 1 J.

B) Synthesis of UMX1

1000 mg of UMX2 were dissolved in 5 mL concentrated H_2SO_4 and added dropwise to a mixture of 7.5 mL 50% w/w H_2O_2 and 25 mL H_2SO_4 at 0 °C. The mixture is stirred at this temperature for 3 h and overnight at room temperature. After diluting the mixture with 100 mL icewater the compound was isolated by filtration and washed with water and dried in air giving 1.00 g of UMX1 (yield: 86 % mol/mol).

The features of the products are as follows:

DSC (5 °C min^{-1}): 205 °C (dec.); **IR** (ATR, cm^{-1}): $\tilde{\nu}$ = 1586 (w), 1566 (w), 1541 (vs), 1471 (w), 1363 (w), 1332 (s), 1300 (m), 1263 (w), 1204 (w), 1084 (w), 1072 (w), 1000 (w), 906 (s), 844 (s), 806 (s), 775 (m), 742 (w), 673 (w), 598 (w); **Raman** (1064 nm, 200 mW, 25 °C, cm^{-1}): $\tilde{\nu}$ = 3007 (11), 1573 (14), 1474 (6), 1453 (12), 1427 (100), 1411 (13), 1368 (35), 1334 (61), 1266 (10), 846 (60), 808 (6), 744 (13), 536 (5), 494 (5), 325 (17), 234 (6); **^{1}H NMR** (acetone-d_6, 25 °C, ppm) δ: 7.84; **^{13}C{^{1}H} NMR** (acetone-d_6, 25 °C, ppm) δ: 144.2, 138.8, 123.8, 67.3; **^{14}N NMR** (acetone-d_6, 25 °C, ppm) δ: -29.1, -31.0, -33.5; **m/z (DEI$^+$)**: 372.1 [(M -NO_2)$^+$]; **EA** ($C_7H_2N_{10}O_{12}$, 418.15): calc.: C 20.11, H 0.48, N 33.50 % w/w; found: C 19.91, H 0.82, N 32.55 % w/w; **BAM drophammer**: 4 J; **friction tester**: 112 N; **ESD**: 0.6 J.

In the above features of UMX2 and UMX1 **EA** means "elementary analysis", wherein "calc." means the calculated and "found" means the actually determined percentage by weight of the respective elements. **m/z (DEI$^+$)** means the result obtained by mass spectrometry using **D**esorption **E**lectron **I**onisation. The result is given as mass (m) per charge (z), i. e. the mass (in atomic mass units) of the molecule having a single positive charge.

Claims

1. Bis(3,4,5-trinitropyrazolyl)methane.

2. Bis(3,5-dinitro-4-aminopyrazolyl)methane.

3. Energetic active mass comprising bis(3,4,5-trinitropyrazolyl)methane or bis(3,5-dinitro-4-aminopyrazolyl)methane or a mixture thereof.

4. Energetic active mass according to claim 3, wherein the energetic active mass comprises or consists of a mixture of bis(3,4,5-trinitropyrazolyl)methane and a powdered metal, in particular aluminum or magnesium.

5. Use of bis(3,4,5-trinitropyrazolyl)methane or bis(3,5-dinitro-4-aminopyrazolyl)methane or a mixture thereof as explosive.

6. Method for synthesizing bis(3,5-dinitro-4-aminopyrazolyl)methane wherein 3,5-dinitro-4-aminopyrazolate anions are contacted with a methylene bridge inducing agent in a solution comprising or consisting of a polar solvent.

7. Method according to claim 6, wherein the methylene bridge inducing agent is diiodomethane.

8. Method according to claim 6 or 7, wherein the solvent is an aprotic solvent, in particular dimethylformamide.

9. Method according to any of claims 6 to 8, wherein the 3,5-dinitro-4-aminopyrazolate anions are contacted with said methylene bridge inducing agent at a temperature of at least 50 °C, at least 60 °C, at least 70 °C or at least 80 °C.

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10. Method according to any of claims 6 to 9, wherein the bis(3,5-dinitro-4-aminopyrazolyl)methane is obtained from the solution by precipitation by reducing polarity in the solution, in particular by addition of water to the solution.

11. Method for synthesizing bis(3,4,5-trinitropyrazolyl)methane wherein bis(3,5-dinitro-4-aminopyrazolyl)methane is oxidized to yield bis(3,4,5-trinitropyrazolyl)methane.

12. Method according to claim 11, wherein H_2O_2, H_2SO_4 or a mixture of H_2O_2 and H_2SO_4 is used as a means for oxidation and as a solvent for said bis(3,5-dinitro-4-aminopyrazolyl)methane and said bis(3,4,5-trinitropyrazolyl)methane.

13. Method according to claims 11 or 12, wherein the bis(3,4,5-trinitropyrazolyl)methane is obtained from a solution comprising or consisting of the solvent and bis(3,4,5-trinitropyrazolyl)methane by precipitation by addition of water to the solution.

Abstract

The invention relates bis(3,4,5-trinitropyrazolyl)methane (UMX1), bis(3,5-dinitro-4-aminopyrazolyl)methane (UMX2), an energetic active mass comprising at least one of these compounds, a use of at least one of these compounds as well as methods for synthesizing these compounds.

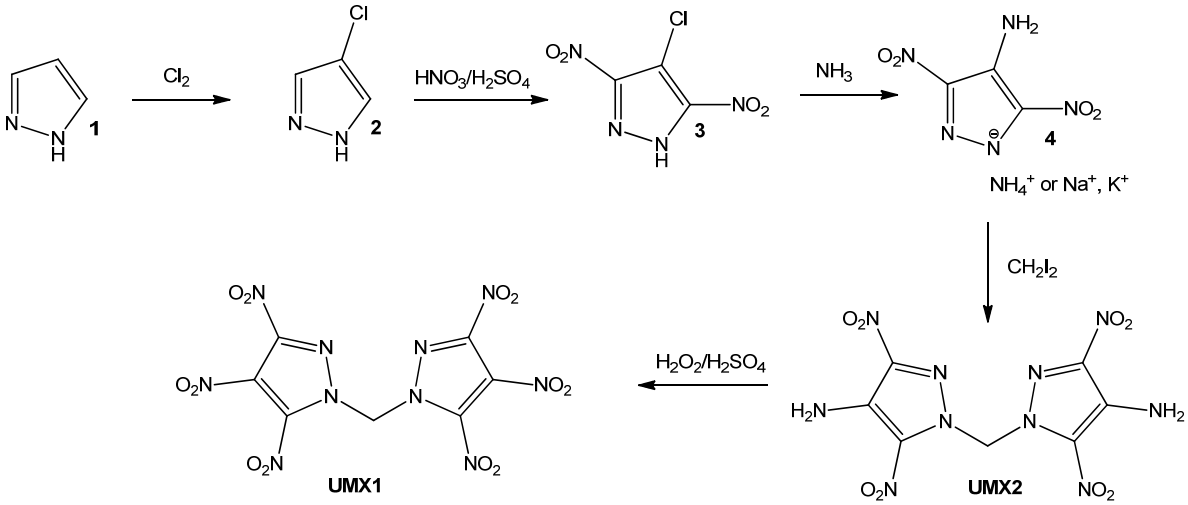

Fig. 1

curriculum vitae

Personal information

Name	Dennis Fischer
E-Mail	dfich@cup.uni-muenchen.de

Education

09/1992 – 07/1996	**Elementary school** St. Max, 86152 Augsburg
09/1996 – 06/2005	**Abitur** Gymnasium bei St. Stephan, 86152 Augsburg
10/2005 – 09/2008	**Bachelor of science in chemistry/biochemistry** at LMU Munich
10/2008 – 10/2010	**Master of science in chemistry** at LMU Munich
03/2011 – 12/2015	**PHD thesis** at LMU Munich in the group of Prof. T.M. Klapötke inorganic chemistry – energetic materials

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Awards

Römer price of the "Dr. Klaus Römer foundation" at the Ludwig-Maximilians University Munich for excellent scientific results in chemistry and biochemistry, **2014**.